

SPUTTERING AND ION PLATING

*The proceedings of a technology utilization
conference held at Lewis Research Center, March 16, 1972*



Technology Utilization Office 1972
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C.

FOREWORD

This Conference on Sputtering and Ion Plating was organized to transfer an awareness of certain selected new technology together with indications of potential applications.

Those presenting papers represented government, university, independent laboratory, service industry, and equipment manufacturing organizations. Thus, in the Conference it was possible to present an overview of the field, brief treatment of concepts, new technology developments, industrial-commercial applications and equipment availability. The last two were supplemented by commercial displays from 27 companies.

The Conference was attended by a large number of industry executives and technical managers from a wide variety of organizations. In part, this is due to the cooperation of various professional societies and trade associations with whom we worked in developing an invitation list. We acknowledge their valuable assistance with thanks and are pleased to list them below.*

The Conference is a part of the continuing NASA effort in technology transfer. To help achieve this transfer, your questions and comments are both invited and welcome; we encourage your direct contact with our Technology Utilization Office.

Bruce T. Lundin
Director
Lewis Research Center

*American Ceramic Society, American Electroplaters' Society, American Gear Manufacturers Association, American Glassware Association, American Institute of Chemical Engineers, American Society of Electroplated Plastics, American Society of Lubrication Engineers, American Vacuum Society, Anti-Friction Bearing Manufacturers Association, Electrochemical Society, Glass Container Manufacturers Institute, Manufacturing Jewelers and Silversmiths of America, National Association of Corrosion Engineers, National Association of Metal Finishers, National Institute of Ceramic Engineers, Piston Ring Manufacturing Group, Plastic Container Manufacturers Institute, Society of Vacuum Coaters.

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I. WHY ION PLATING AND SPUTTERING?

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The question "Why ion plating and sputtering?" is rather easily answered for those interested in lubrication. It was, of course, the lubrication problems that motivated our use of these processes (ref. 1). In particular, our interest in vacuum methods is for depositing solid lubricants. In the present circumstance we would like to extend the interest in ion plating and sputtering to technical areas beside solid film lubrication. We hope to stimulate interests for other fields by telling you of our experiences in lubrication and providing added background.

The primary means of depositing useful surface films as used at the Lewis Research Center are summarized in table I-1. The basic and more

TABLE I-1. - COMPARISON OF SPUTTERING AND ION PLATING

Sputtering	Ion plating
Nonevaporative	Evaporative
Momentum transfer (atoms)	Direct transfer (ions)
Kinetic energy of order of 50 eV	Kinetic energy generally 3000 to 5000 eV
Specimen near ground potential	Specimen at high voltage
Sputtered atoms (plate complex surfaces)	Evaporant ions-electric lines of force (plate complex irregular surfaces)
Reproducibility (composition, thickness, uniformity)	Reproducibility (composition, thickness, uniformity)
Flexibility (metals, polymers, ceramics)	Metals, alloys

generally applied aspects of these processes, the equipment used, and some performance data are described more comprehensively in subsequent papers.

Experience with the sputtered and ion plated lubricating films has shown outstanding performance (ref. 1). Some of the characteristics of the lubricating films suggest that there are wide areas of usefulness. Our view of the likely range of utility is represented by the diverse interests of the invited attendees for this meeting. Chemical, metal processing, packaging, electronics and personal products manufacturers as well as those concerned with lubrication, friction, and wear have been asked to participate.

The primary objective of this discussion is to develop some of the reasons for our interest in these vacuum coating processes for lubrication and to provide some introductory background for the presentations that follow.

THIN FILMS IN LUBRICATION

It has long been very clear that thin surface films are critical to friction, wear, and lubrication (refs. 2 and 3). As figure I-1 shows, so-called boundary lubricating films may be only a few millionths of an inch thick. Operating in any media, adsorbates will usually form on solid surfaces. Typically, the adsorbed films may be moisture or polar compounds from organic lubricants oriented normal to the surface in mono-molecular films around 20 \AA ($80 \times 10^{-9} \text{ in.}$) thick. There are, however, some evidences of ordered films with thicknesses to 2000 \AA ($8 \times 10^{-6} \text{ in.}$). With the load between surfaces in relative motion, contact occurs at the high spots. As motion progresses the adsorbed films are sheared; they provide low friction as long as they are not destroyed by the heat generated in shearing or simply displaced by the very high but localized surface stresses. It must be appreciated that the real contact areas are determined by the loads applied and the compressive yield stress of the weaker substrate material.

At some point with increased loading or shear the adsorbed film is penetrated. Also, in a vacuum such as that of space there may be no source of adsorbate. Then the surfaces may still be protected by another type of film that is usually present on metal bearing materials. Oxide films from 20 to several thousand \AA thick are typical, or other types of reaction films may be present. Again, if that film is worn or stressed sufficiently, it may

be penetrated. When the bare (nascent) surfaces are in contact with one another under even very light loads, they will adhere or weld. With continued motion, the friction process is one of shearing metallic junctions. Shearing may occur at the original surface or within the bulk of subsurface material. The sheared junction becomes work hardened, and transferred material that is very hard may protrude from one surface to serve as a cutting tool or break loose and function as a loose abrasive particle. This is the most common process in wear: initiation by adhesion and shear followed by abrasion by fixed or loose hard particles. There are also a number of other mechanisms of wear beside adhesive and abrasive wear: the most prevalent of the others is corrosive wear.

In our present context we are concerned with providing performed surface films by sputtering or ion plating. Such films should prevent contact between nascent base materials, should shear with minimum force, and should be very difficult to displace and hopefully to protect against corrosive wear.

EFFECT OF FILM THICKNESS

The first widely known data on the effect of film thickness of solid lubricating films were reported by Bowden and Tabor (ref. 2). Those data (fig. I-2) were for indium coatings on steel. An optimum thickness for minimum friction was found. The increasing friction observed with the greater film thickness was shown to result from an increase in contact area. With film thickness less than optimum, higher friction was observed; it was indicated that this resulted from a lack of uniformity of the coating thickness although asperity penetration of the film is likely (ref. 4). Areas of the surface were inadequately covered by the film, and the friction was the result of partial solid substrate shearing and partial lubricant film shearing. Because of the markedly higher shear strength for the base metal, very small amounts of substrate to substrate contact could have substantial influence on friction.

Similar data can be developed for any solid lubricating material. The level of friction depends on the shear resistance of the film and the shear resistance of the exposed substrate material; with very thin films the yield

strength in compression of the substrate material primarily determines the area being sheared.

Reference 4 suggests that the friction begins to rise when the ratio of the film thickness to the roughness of the substrate approaches unity. This hypothesis has been substantiated with indium but exceptions were noted for extremely thin films. The assumption that the film thickness must be greater than the surface asperity peaks is based on bulk flow properties of the coating materials. Thus, with substantial film thickness, adhesion of the film to the substrate is likely mechanical and bond contamination can be tolerated because lost film material can be replaced by plastic flow from the adjacent film.

It is suggested that for many solid lubricant films the adherence to the substrate is very weak. When that film is subjected to a shearing stress, slip is more apt to occur at the film-substrate interface than in the film. It is in such situations that film thickness greater than asperity height is needed to ensure the reformation of a protective film by plastic flow of the film; otherwise, subsequent contacts would be with uncoated asperities and friction would increase.

Where there is a chemical or diffusion bonded or other transition layer at the film-substrate interface the chance of shear at that interface is reduced. As will be discussed in the later papers, such highly adherent films are generally advantageous.

The very good adherence of ion plated and sputtered coatings makes them particularly attractive in lubrication. Shear occurs in the film where it belongs during sliding rather than at the film-substrate interface. Thus, with the vacuum deposition methods we are considering, film thickness can be much less than asperity height without the danger of shear at uncoated surfaces. Friction continues to decrease with decreasing film thickness as illustrated by the dashed line extrapolation of figure I-2. With initial operation the film is compressed, sheared, and otherwise reduced in thickness and lower friction is achieved. Operation also provides desired orientation of the thin film grains and crystallites.

The other primary justification for using films of substantial nominal thickness is because of nonuniform film thickness. That is, to be sure that at least the minimum needed film thickness for surface protection is present on all surface contact areas, the usual thickness had to be much greater.

With the vacuum deposition methods considered in this symposium, thickness control is so precise as to eliminate the factor of poor process control in optimizing the nominal film thickness.

Effect of Temperature on Solid Lubricants

The temperature limits for the use of solid lubricants are most often a function of the bonding media. Figure I-3 shows data for MoS_2 compared with graphite monofluoride and CaF_2 . In this case the data for MoS_2 are of primary concern since the MoS_2 is very often deposited by vacuum methods. The current curve represents data obtained with a conventional bonding agent. The potential curve is that for MoS_2 alone and failure results from its oxidation. It is clear that improved high temperature performance is possible if no bonding agent is needed. The vacuum deposition methods do not require a bonding agent and therefore may provide improved lubricating films for higher temperatures. In cases where endurance requirements are not stringent, burnished films may also be adequate at high temperatures.

LIMITATIONS OF OTHER COATING METHODS

The problems with other types of coatings have been intimated in preceding discussions. They are associated with nonuniformity of film thickness, the need for greater film thickness, and the limitations imposed on a desired lubricating material by the binding agent.

Figure I-4 is presented to illustrate the adherence problem rather uniquely. This shows a flat surface of a disk friction specimen which had an electroplated silver film on its surface after a friction experiment and subsequent sustained heating in a vacuum system bakeout. Contaminants diffused from the base metal and at the interface caused blisters to occur in the silver plating during heating in vacuum. Such contamination does not occur in the vacuum deposition processes.

To illustrate the use of ion plating for friction surfaces in mechanical components, some 125-millimeter ball bearings were run that had ion plated silver on cages. In operation to extreme bearing temperatures (e. g. ,

700° F) the cage coatings were never a cause of failure. It must also be mentioned, however, that electroplated silver is also widely used and usually effective in this application. The point here is that no unusual deficiencies were found for the vacuum coated silver films, which were much thinner than electroplated films.

The thermal and mechanical stresses that have been imposed on the vacuum deposited coatings under consideration have been extremely severe. The range of application for such coatings within the limitations of the particular coating material is greater than for any other coating method we have considered. The economies of effective thin films may allow the use of coating materials too expensive for other methods that require thicker films.

CONCLUDING REMARKS

Why vacuum deposition methods for solid surface films are attractive to lubrication can be summarized in a few words: (1) outstanding adherence, (2) no bonding agent needed, (3) extremely thin films are successful, and (4) exceptional film thickness uniformity. The economies are significant when 1 cubic inch of coating material will allow coverage of 2 million square inches to a useful thickness of 2000 Å.

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BOUNDARY FILMS

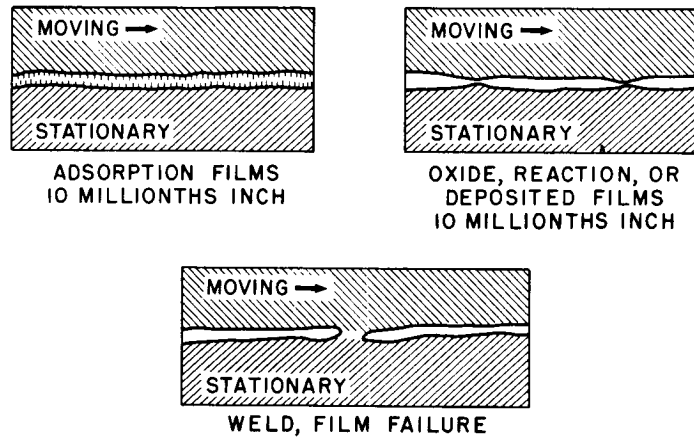


Figure I-1

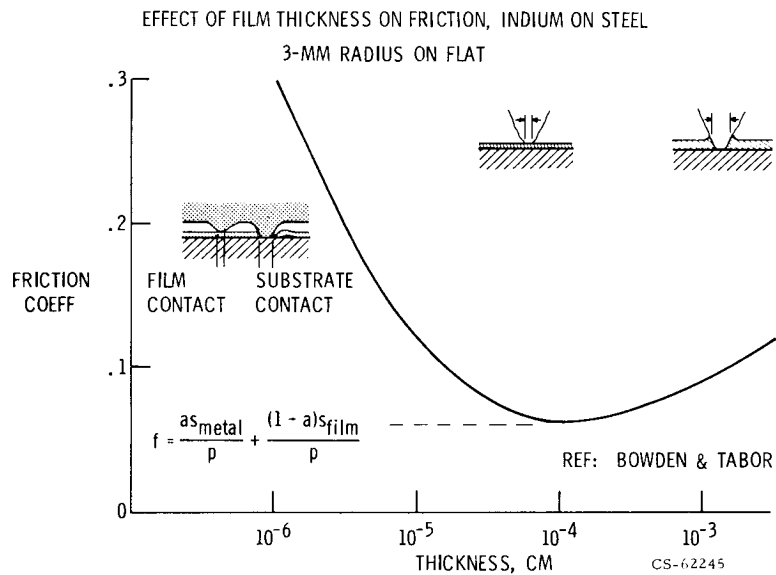


Figure I-2

EFFECT OF TEMPERATURE ON SOLID LUBRICANTS

THIN BONDED FILMS - IN AIR - 440C OR INCONEL

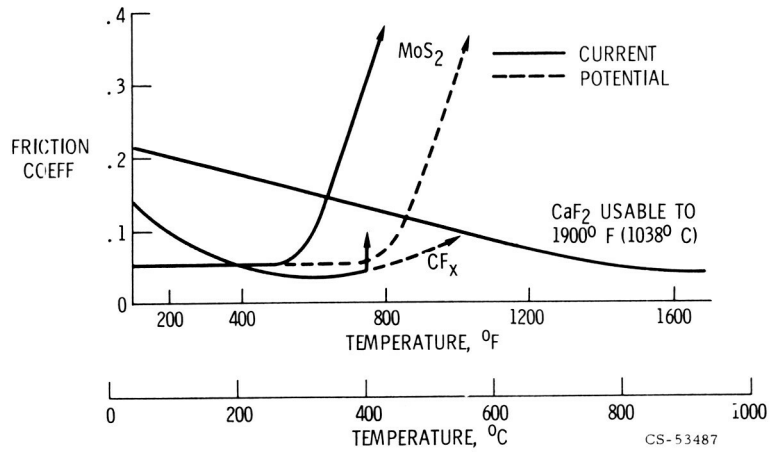


Figure I-3

BLISTERING OF ELECTROPLATED SILVER (.001") ON 440C AFTER
STANDING IN VACUUM (10^{-9} mm Hg) AT 400° F FOR 16 HOURS

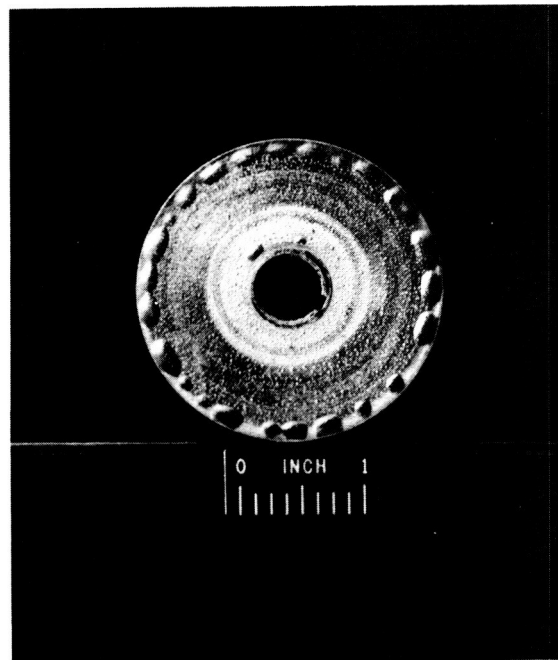


Figure I-4

II. ION PLATING - CONCEPTS AND APPLICATIONS*

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The adhesion between components of a system depends on three factors: the chemical bonding across the interfacial region, the type of interfacial region, and the fracture mechanism which results in failure. In most cases, one must rely on chemical bonding to obtain good adhesion. One key to good adhesion is to bring atoms into intimate contact over a large area. In the case of deposited films good adhesion also means that the surface must be free of contaminants which prevent intimate contact or which may have low strengths and that the nucleation and growth of the films must be such that there is a high interfacial contact area.

Obtaining good adhesion means that one must control the surface condition and the type of interface which is formed between the materials. Controlling the surface condition may involve:

- (1) Cleaning - to remove contaminants
- (2) Surface modification - to change the character of the surface
- (3) Use of adhesion promoters or "primers" - to create a new surface for deposition or to influence the nucleation of the depositing material

Cleaning may involve a chemical solvent to remove organics, a chemical etch to remove surface layers (such as oxides), thermal desorption to remove volatiles, hydrogen firing to reduce oxides, oxygen firing to oxidize contaminants, or sputter cleaning to remove surface layers by sputtering. Usually, the cleaning operation is distinct from the coating process and only removes gross contamination.

*This work supported by the U. S. Atomic Energy Commission.

Surface modification may be in the form of changing the physical characteristics of the surface by extensive etching or abrading. Surface modifications may affect the failure mechanism of an interface by eliminating voids, etc.

The use of a primer to promote adhesion is common in organics where polar adsorption is important. But primers are also widely used on metals and ceramics where an intermediate layer is used between the coating and surface either to provide a material that will bond to both the coating and the surface or to influence the nucleation and growth of the coating.

The presence of good bonding does not necessarily mean that there will be good adhesion in service. The fracture mechanism may be the controlling factor. For instance, if the interface is brittle and there are stress concentrators, such as voids, failure may occur at low stress levels, even though the chemical bonding is extensive.

The type of interface often determines the fracture mechanism. For instance, the interfacial region may be either continuous or porous. A porous interfacial region generally will be weaker because the pores act as stress concentrators and decrease the effective interfacial area. An example of this type of interface is in the aluminum-gold system where Kirkendall porosity gives rise to a weak interface and poor strength (ref. 1). Nucleation and growth processes of films can give porous interfaces when isolated nuclei must grow to appreciable size before the film becomes continuous and do so without "wetting" the substrate surface (ref. 2).

Another way to define interfacial structure is to consider the regions in contact. The types of interfaces then may be categorized as (ref. 2) mechanical, monolayer-to-monolayer, compound, diffusion, or "pseudodiffusion."

The mechanical interface may be formed if the surface contains large pores. In this case, the film material fills the pore and mechanical interlocking provides the adhesion. No chemical reaction between the materials is necessary, and the adhesion depends on the physical properties of the materials.

The monolayer-to-monolayer type of interface is characterized by an abrupt change from the film material to the substrate material in a distance on the order of the separation between atoms (2 to 5 Å). This type of interface will be formed if there is no diffusion of the depositing atoms into the

substrate surface. With this type of interface, the stresses between the film and substrate material will be locally confined.

The compound interface is characterized by a region of constant composition. The compound is formed by the interaction of the film and substrate material and may be an intermetallic compound, or some other chemical compound, such as an oxide. The intermetallic compounds formed from two metals are usually brittle and easily fractured. In the compound interface the stresses are principally concentrated in two areas, between the film and compound and between the compound and the substrate material.

The diffusion interface is characterized by a gradual change in composition across the interfacial region between the film and substrate. The formation of this type of interface requires that there be diffusion between the film and substrate material, which means that there must be some degree of solubility and that energy must be available for diffusion. In this type of interface the stresses are distributed throughout the interfacial region, which may be thousands of angstroms in extent. Essentially, the interface is "graded" from the substrate material to the film.

The term "pseudodiffusion" may be used to designate the interfacial region formed under high-energy conditions. This type of interface will be formed if two molten materials in contact are mixed and then quenched as in the case of fusion welding. Another example is the interfacial region formed by particles impinging on a surface with sufficient kinetic energy to penetrate into the substrate lattice without the need of a diffusion mechanism. This type of interfacial region allows the grading from one material to another without the need for diffusion. Of course, a typical interface may be composed of a combination of several types of interfaces. For instances, a combination of mechanical, compound, and diffusion interfaces.

The most desirable type of interface, from the standpoint of adhesion, is one in which stresses in the interfacial region are distributed over an appreciable volume without the generation of a low strength or brittle region. This can best be done by grading the composition of the interface from that of the bulk material to that of the coating material. This grading can be accomplished by allowing extensive diffusion and chemical reaction in the surface region or by controlling the composition of depositing material by codeposition, or by reactive deposition techniques (ref. 3). All these techniques are useful in specific circumstances. The most common procedure for

forming a reaction interface is by bulk heating the part to be coated to promote diffusion and chemical reaction. In some instances, this cannot be done because of the thermal sensitivity of the material or because of the presence of barrier layers, or because the materials are insoluble. In these cases, other techniques may be useful. Of these, the process called "ion plating" (refs. 4 and 5) has been found to be particularly useful in coating incompatible metal systems.

ION PLATING

Ion plating is a generic term applied to atomistic deposition processes in which the substrate is subjected to a flux of high energy ions sufficient to cause appreciable sputtering before and during film deposition. The ion bombardment is usually done in an inert gas discharge system similar to that used in sputter deposition, except that in ion plating the substrate is made a sputtering cathode. The substrate is subjected to ion bombardment for a time sufficient to remove surface contaminants and barrier layers (sputter cleaning) before deposition of the film material. After the substrate surface is sputter cleaned, the film deposition is begun without interrupting the ion bombardment. For a film to form it is necessary that the deposition rate exceed the sputtering rate. From the standpoint of adhesion, the principal benefits obtained from the ion plating process are ability to (a) sputter clean the surface and keep it clean until the film begins to form, (b) provide a high energy flux to the substrate surface giving a high surface temperature, thus enhancing diffusion and chemical reactions without necessitating bulk heating, and (c) alter the surface and interfacial structure by introducing high defect concentrations, physically mixing the film and substrate material, and influencing the nucleation and growth of the depositing film.

Sputter cleaning has been shown to be the most universal technique for obtaining atomically clean metal surfaces in a vacuum environment (ref. 6). The ion bombardment associated with sputter cleaning disrupts the surface structure (ref. 7) and introduces a high concentration of point defects (refs. 8 to 10). Sputter cleaning must be done in a gaseous environment relatively free from contaminant gases. The amount of contaminant gases that can be tolerated depends on the material being sputter cleaned. For instance, the

surface of a reactive material having a low sputtering rate may be further contaminated by attempting to sputter clean the surface with a gas containing appreciable reactive gases. This technique may be used to form oxide and nitride surfaces in a gas discharge. On the other hand, a metal such as gold can be effectively cleaned using oxygen since it does not appreciably react with the gaseous environment.

One way of monitoring the sputter cleaning portion of the ion plating process is by monitoring the current in the discharge with the gas pressure and voltage kept constant. Since the discharge current consists partially of secondary electrons emitted from the bombarded surface, the current is sensitive to the surface condition. Metal oxides generally have a higher secondary electron emission coefficient than does the metal, so the discharge current decreases as the metal surface is cleaned of oxides. Figure II-1 shows this effect in cleaning uranium surfaces at varying gas pressures as a function of time (refs. 11 and 12). The equilibrium value is taken to be a clean, or at least reproducible, surface. Thus, the current behavior along with the partial pressure of reactive gases in the system may be used as a process control for sputter cleaning of the metal.

Sputter cleaning results in a very reactive surface can be rapidly contaminated if exposed to reactive gases. For instance, a partial pressure of 10^{-6} torr of oxygen will form a monolayer of oxide on a metal surface in about 1 second if the sticking coefficient is unity, and a few monolayers of oxide can drastically alter the diffusion process. For this reason, maintaining an atomically clean surface for any appreciable time requires a very good vacuum, and a very good vacuum is often not compatible with industrial processing.

For insulators and plastics, exposure to a plasma may result in surface changes that give better adhesion. In the case of insulators, ions are accelerated across the wall sheath and "ion scrub" the surface (ref. 13). For plastics, exposure to a glow discharge can give a more bondable surface ("CASING" technique, refs. 14 and 15), and it is thought that ultraviolet radiation from the plasma is a primary cause (ref. 16).

The rate of chemical reaction and diffusion at a clean surface depends on the temperature and defect structure of the surface region. In ion bombardment, most of the ion energy is given up in the form of heat as the ion is stopped in the surface region. The ion penetration is roughly 50 \AA/keV ,

so the heating is confined very close to the surface. This means that the bulk of the material can be kept at a low temperature while the surface may be very hot, depending on the thermal transport properties of the system.

Structural defects act to increase the value of the diffusion coefficient (ref. 17). In addition, a very high concentration of defects may alter a normally insoluble two-component system to one where there is a degree of solubility.

In the ion plating process metal atoms are injected into the gas discharge, and it is to be expected that a portion of these are ionized, primarily by a Penning ionization¹ mechanism and accelerated to the substrate. In most cases, the metal ion flux will be much less than the metal atom flux, so this mechanism is not considered to be important in the usual case. In special cases where the ionization is appreciable and energies are high, the metal ion bombardment may be important to the generation of good adhesion (refs. 19 to 22). Metal ionization can be enhanced by designing the vapor source so as to increase electron-atom collisions and by using a gas such as helium which has high metastable energies. The good adhesion normally found with sputter-deposited films has been attributed to the high energy of the sputtered atoms (ref. 23).

Another effect is the return of sputtered particles to the target surface. The majority of sputtered particles are neutral - some of these neutrals are ionized in the discharge and return to the target, while some of the neutrals are scattered back to the target surface. These effects are not generally considered to be important in the ion plating process, though they may be important if the deposition rate is low and the sputtering rate is high as the interfacial region is being formed. This might be the case where the substrate potential is slowly decreased to the point where a film is allowed to form.

All these processes that occur in ion plating tend to form an interfacial region conducive to good adhesion. Another effect found in ion plating, which

¹Penning ionization: The ionization of an atom by the transfer of the excitation energy from a metastable atom whose excitation energy is greater than the ionization energy of the first atom. For example, argon has metastable states of 11.55 and 11.75 eV; the ionization energy of copper is 7.68 eV. Thus a copper atom colliding with a metastable argon atom is easily ionized. (For a further discussion see ref. 18.)

is often useful, is the scattering and entrainment of the film atoms in the gas discharge (refs. 24 and 25). This effect tends to give a uniform coating over a complex surface out of the line of sight of the vapor source as does sputtering from the ion-bombarded substrate surface (refs. 26 to 28). Figure II-2 shows the results of ion plating on a cylinder from one direction. A rather uniform coating is formed over the outside of the cylinder, and film material is "thrown" to an appreciable depth in the bore of the cylinder.

It has been shown that the presence of a gas discharge influences the nucleation of the films on surfaces (ref. 29). In general, it is found that the nucleation density is increased and that the film becomes continuous at lower thicknesses when a discharge is present than when the deposition is done by vacuum evaporation. This is attributed to electric-field effects and the higher energy of the depositing atoms. Surface cleanliness and heating are probably also important factors.

An effect that has not been studied very extensively is the effect of ion bombardment on the morphology of the growing film. It has been shown (ref. 30) that for the deposition of refractory metals, ion bombardment during deposition can change the normally columnar morphology to a more dense isotropic structure. There is probably a complex interrelation between coating morphology, deposition rate, and ion bombardment. It has been found that the deposition of high-energy particles can lead to the growth of epitaxial films at low temperatures (refs. 31 to 33) and the growth of unusual phases (ref. 34). It is often observed during high-rate ion plating that the surfaces in the system that are not subjected to ion bombardment receive a fine particulate deposit similar to that produced in gas evaporation (refs. 35 and 36). This is apparently due to gas phase nucleation of particles. These fine particles acquire a negative charge in the discharge and may be collected by inserting a positively charged plate in the discharge.

TECHNIQUES

Figure II-3 shows a simple ion plating setup. This system is continuously pumped by a vacuum system capable of attaining a vacuum sufficient to reduce the levels of contaminating gases, normally to the 10^{-7} torr range.

The surface to be coated is made the cathode of a diode type of dc gas discharge system, and the high-voltage lead to the part is carefully shielded to prevent metal deposition on the insulator during the plating operation. The anode of the discharge circuit is attached to the metal deposition source, in this case, a resistively heated evaporation filament. A high-voltage dc power supply having a high reactance, such as is normally used for sputtering, is used in ion plating. A resistor and recorder in series with the high voltage circuit are used to monitor the current in the discharge. The gas inlet is through a variable leak, and the pressure in the system is monitored by means of a capacitance gage.

In a typical operation, the part is precleaned and placed in the vacuum system. The system is then evacuated to an ultimate of 5×10^{-7} torr and the evaporant premelted. Next, the system is backfilled with argon to a pressure of 10 to 50 millitorr, and the dc gas discharge is established at 2 to 5 kilovolts and a 0.5-milliampere-per-square-centimeter cathode current density. The part is then sputter cleaned for a period of time, which depends on the material and surface condition. At the end of the cleaning portion of the process, the evaporator filament temperature is slowly raised until the material begins to evaporate. A shutter between the source and substrate is then opened, allowing the material to deposit on the substrate. The important step is to form the surface-coating interface during the ion bombardment. After the interfacial region is formed, the system may be evacuated and the film thickness increased by vacuum evaporation.

In the simplest procedure, ion plating is done in an inert gas discharge, usually argon. Lighter inert gases require higher pressures to maintain a discharge and give lower cleaning rates; with heavier inert gases, the diode discharge can be maintained at lower pressures, and the cleaning rates will be increased at a given current density. It is important to use a continuously pumped system to prevent the contaminants, which are sputtered from the surface, from recontaminating the part.

In the simplest case, the part is connected directly to the high-voltage lead. In other cases, the part is held by a holder, which may be cooled or heated. A ground shield is placed around the cathode at a spacing less than the cathode dark space width. This shield confines the ion bombardment to the surface to be plated. Care must be taken to prevent the ground shield from shielding a portion of the surface from ion bombardment. Figure II-4

shows a substrate arrangement in which the part to be plated is in contact with, or embedded in, a shielded cold finger (ref. 37). This type of holder is useful if one wishes to keep the substrate cold to prevent decomposition, limit diffusion, or maintain a given heat treatment through the bulk of the part. In this case, the surface is subjected to the high-energy flux, but the bulk of the part is maintained at a low temperature. Figure II-5 shows a setup to coat a complex part. In this case, the part is freely suspended with no cooling.

There are three main problems with making the substrate the cathode in the discharge: (1) a shielded high voltage lead must be attached to the part in such a manner as not to be shorted during the deposition (ref. 38), (2) shadowing of the substrate surfaces by improper shielding, and (3) overheating due to geometrical effects. A common mistake is to use a bare wire to provide high voltage connections. In this case, the wire provides a high field area and much of the energy in the discharge is wasted in ion bombardment of the wire as well as causing the wire to melt or erode rapidly. Improper placement of shields around the substrate may shadow part of the surface from ion bombardment. Holes and reentrant areas on the substrate give rise to locally higher density plasmas due to the trapping of secondary electrons. This in turn increases the local heating on the part. Another problem is contamination of the part by sputtered material from the holder. This can be overcome by coating the holder with an appropriate material before deposition.

Figure II-6 shows a variety of methods of providing the vapor to be deposited. Each technique has its advantages, disadvantages, and uses. The technique of using a metal-bearing gas as a vapor source may be compared to chemical vapor deposition and has been termed "chemical ion plating" (refs. 39 to 41). The electron beam heating technique (refs. 42 and 43) provides the ability to deposit refractory materials and large quantities of materials easily. Often, when using a sputtering target to provide the film material, it is necessary to continuously decrease the potential on the substrate so that at some point the deposition rate becomes greater than the removal rate. This is particularly true when depositing an easily sputtered material such as gold. When using a sputtering target as a vapor source, the process is very similar to bias sputtering (ref. 3) except that the ion plating potential is usually much higher and the object of the process is somewhat different.

In bias sputtering, the principal object is to bombard the growing film with relatively low energy (50 to 300 V) ions to cause desorption of contaminating gases and give a more pure deposit. Sometimes in bias sputtering a positive bias is applied to the film during the initial formation of the interfacial region as it is found that adhesion may be poor if the contaminate gases are excluded from the interface (refs. 44 and 45). In some cases, special ion sources have been constructed which provide beams of metal ions for deposition (refs. 22, 34, and 46). Flash evaporation has also been used as a source for alloy deposition (ref. 47), and plasma sources have been used to vaporize and partially ionize the film material (ref. 48).

In most cases, the potential applied to the metal substrates should be several thousand volts and the current density should be several tenths of a milliamperere per square centimeter in order to have a good sputter cleaning rate. The substrate potential may be dc or rf. Normally, dc is used for conductive surfaces and a separate power supply is used. An rf potential may be used with conductive and insulating surfaces. An interesting phenomena is the fact that a relatively low rf potential on the surface can often give a high sputtering rate of depositing film material, seemingly much more so than an equal dc potential. A negative substrate potential of about a hundred volts can be generated by "tuning" the substrate with respect to ground and the plasma (ref. 49). Higher potentials require a separate power supply.

Results with a bias on or near an insulating surface have given erratic results. In some cases no increase in adhesion is found when as rf bias is applied to the insulator (ref. 39), but in other systems adhesion is greatly enhanced (refs. 39 and 51 to 54). I suspect that the difference is to be found in changes in the nucleation stage of films deposited on insulator surfaces in a gas discharge (refs. 50 and 55). This may be particularly true for deposition of metals on plastics (refs. 22 and 56).

APPLICATIONS

The bibliography of this paper consists of published works utilizing the ion plating process or processes very similar to it and indicates the materials involved, where applicable. The papers cover a number of different

areas with a wide variation in completeness of understanding and description. Using the most general definition of ion plating (i. e. , ion bombardment before and during deposition) to create a desirable interface, I would like to choose several representative examples and examine them in some detail.

The area of metals-on-metals will be covered more thoroughly later in this conference when lubrication is discussed, but, since we have rather extensively studied the technology associated with one such system, I would like to discuss it now.

Uranium-Aluminum

The coating of uranium with aluminum for corrosion protection has proved to be an effective solution to a difficult problem (refs. 11, 12, 57, and 58). Previously, enriched uranium components of pulse nuclear reactors were nickel electroplated to provide corrosion protection in the rather severe thermal and mechanical shock environment presented by the pulsing the reactor. After a period of operation, the plating spalled, allowing severe corrosion as shown in figure II-7. This in turn presented a health hazard and required shutdown of the reactor. This problem thus presents the factor that limited the operational life of the reactor components. A survey of possible ion plated coating materials (ref. 59) showed that aluminum was the most probable candidate because of its protective ability, low neutron cross section, high thermal conductivity, and an electronegativity close to that of uranium, thus limiting galvanic corrosion.

The reactor elements presented a variety of massive configurations. Figure II-8 shows a mock-up of the assembled elements. After stripping the nickel coating from the elements, the parts were assembled into coating fixtures such as shown in figure II-5. The system was then evacuated to $<10^{-6}$ torr, the aluminum premelted, argon introduced, and the parts sputter cleaned. The aluminum source was stranded tungsten wire filaments, aluminum chips, and tantalum wire coils to hold the molten aluminum in place.

The sputter cleaning was monitored by the technique described previously and shown in figure II-1. It was found that diffusion at 600°C after

deposition greatly decreased the number of pinholes found in the 0.2- to 0.5-centimeter thick aluminum coating. An interesting point from the standpoint of technology was that initially, sufficient contaminants were deposited on the heater filaments during sputter cleaning and redeposited on the uranium during filament heating to prevent subsequent diffusion. Typically, this problem would be overcome by introducing a shutter, but because of the complex geometry, this would have been difficult. The problem was overcome by maintaining the filament temperature just below the melting point of aluminum during the sputter cleaning operation.

Figure II-9 shows an element after plating and figure II-10 shows the interface structure in the uranium-aluminum coating system. It was determined that the UAl_2 and UAl_3 compounds formed at the interface were probably the most effective source of corrosion protection in the system.

This coating and coating technique has been adapted as a standard for coating uranium and uranium alloys for pulse reactor applications, and several organizations other than Sandia have routinely used the technique for that purpose.

Chemical Ion Plating

Chemical ion plating (CIP) was initially evaluated for the deposition of tungsten at low temperatures (refs. 39 and 40) and was later adapted to the deposition of carbon and other materials available as gaseous species. In CIP, a metal or compound is deposited when the gaseous species is decomposed or reacted either in the vapor or at the ion bombarded surface.

Reference 40 describes the use of the CIP technique to deposit coatings that have low secondary electron emission on grid structures for electronic applications. This application uses not only the interfacial and reactive concepts of ion plating but also the geometrical coverage aspects. A filament supply may be used for a portion of the deposited material or a purely gas system as shown in figure II-11 may be used. In one use of the latter procedure, the gases argon, $TiCl_4$, and C_2H_2 are used. The argon acts to maintain and stabilize the discharge, the $TiCl_4$ supplies titanium metal, and the C_2H_2 provides the carbon. The byproducts of hydrogen, chlorine, and HCl are pumped away.

Coatings containing carbon with titanium, chromium, zirconium, and silicon have been deposited on molybdenum, copper, tungsten, and tantalum. The coatings are of an undefined structure, probably because of a very fine grain size. One big advantage of the coating system is that it is not necessary to heat the wires to high temperatures which, in the case of the refractory metals, causes the wires to become brittle.

Platinum Silicide on Silicon

A recent application of interface formation by ion plating is in the deposition of PtSi contacts on silicon devices. Normally, these types of contacts are formed by sputtering or evaporation of platinum and vacuum sintering to form PtSi by a solid-state diffusion reaction. Reference 60 indicates that the desired PtSi with no other phases can be formed during sputter deposition by subjecting the silicon to an rf potential sufficient to resputter excess platinum (termed continuous backsputter (CBS) technique), leaving only the PtSi interfacial region.

Several other important points about this system should be noted in context with our ion plating discussion (ref. 61). One, there is an enhanced arrival of the Pt at the silicon surface with applied voltage. This is attributed to an entrainment of the Pt atoms in the discharge or possible to the collection of Pt^+ ions. A second point is that, by resputtering during deposition, the deposition of the Pt can be confined to an exposed silicon surface and platinum is not deposited on areas covered by SiO_2 films.

Applications

In addition to the applications listed in the bibliography there have been a number of uses that have not been publicized. Those that I know of are (1) coating beryllium with aluminum for bonding (several mils thickness aluminum), (2) coating molybdenum with gold for bonding, (3) gold on tantalum thin-film circuits for electrical contact, (4) gold on steel for lubrication, (5) aluminum on steel for corrosion protection, (6) nickel on titanium for brazing, (7) cadmium on steel for corrosion protection, (8) silver on

steel for reflecting surfaces, (9) gold on aluminum for electrical contacts, (10) copper on tungsten and tantalum for subsequent electrodeposition.

SUMMARY

Regardless of how one wished to define the ion plating process, the fact remains that the concept of forming a desirable type of interface by subjecting the surface to ion bombardment both before and during film deposition remains a useful concept. The application of this technique has to be evaluated in light of each application, but since it generally requires no equipment other than what may be found in any sputtering/evaporation laboratory, it is an easy tool to acquire. Special applications, such as chemical ion plating, do require some specialized equipment not ordinarily found in chemical vapor deposition laboratories. Ion plating techniques have been applied to deposition of metals, alloys, and compounds on metal, insulator, and organic substrates ranging in size from large reactor elements to small screws and bearings (ref. 62). In many instances, the technique has proved to give superior results compared with more conventional techniques. Therefore, it should be considered for use in any film-substrate system where adhesion may be a problem.

A word of caution should be injected about using the technique when depositing compounds, alloys, and glasses. In these cases the continued ion bombardment of the depositing film may radically change the composition or properties of the deposit (ref. 63). The continued ion bombardment during deposition may also increase the macroscopic stress in deposited metals (ref. 30). If these problems are observed, it may be well to confine the ion bombardment to the formation of the interfacial region and build up the deposit by some other means.

ACKNOWLEDGMENTS

The author would like particularly to acknowledge the contributions of R. D. Bland of Sandia Corporation in the application of the ion-plating process to many problem areas. He would also like to thank investigators in

other laboratories for sharing their experience in using ion-plating processes. In addition, he would like to acknowledge the tolerance of the thin-film community in accepting the ion-plating terminology and regrets any hard feelings that the problem of semantics may have incurred (ref. 5).

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SPUTTER CLEANING TIME OF URANIUM AS FUNCTION OF CATHODE CURRENT DENSITY
AT PRESSURES (REF. 10)

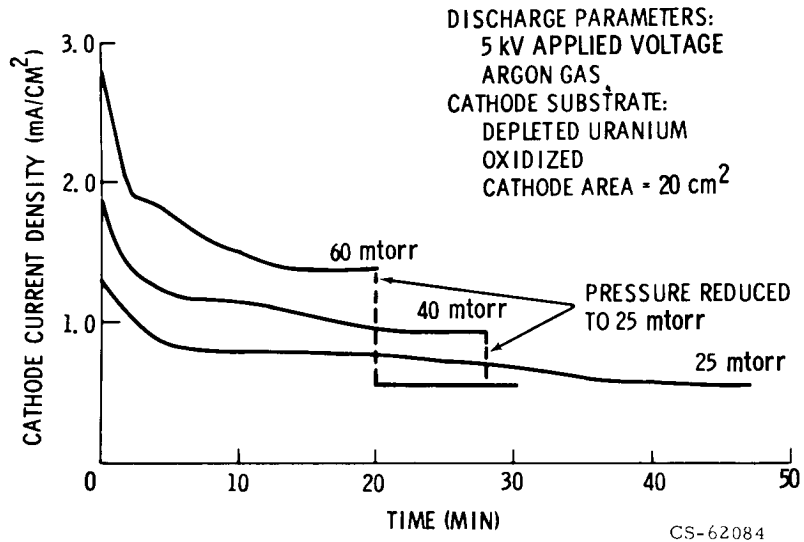


Figure II-1

VARIAION OF COATING THICKNESS OVER A CYLINDRICAL SUBSTRATE (REF. 43; ALL
DIMENSIONS ARE IN MILS UNLESS OTHERWISE NOTED.)

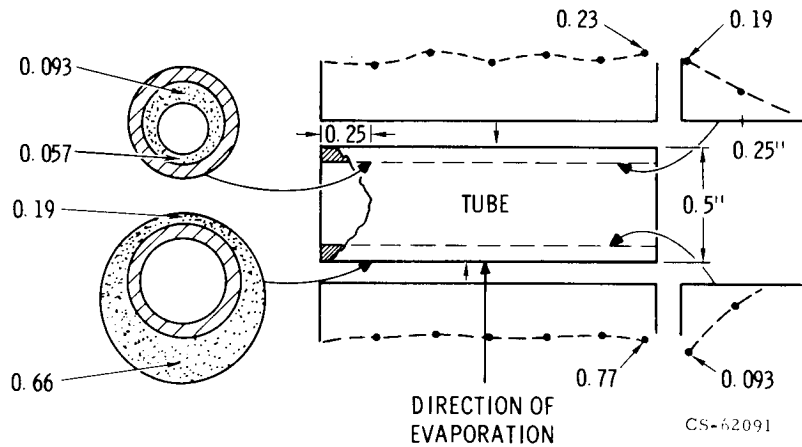


Figure II-2

SIMPLE ION PLATING SETUP USING DC DISCHARGE AND THERMAL EVAPORATION
AS MATERIAL SOURCE

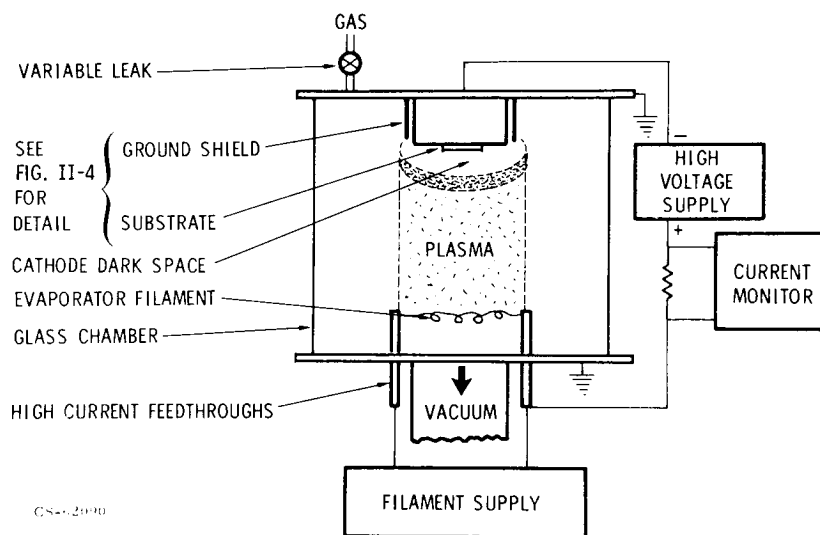


Figure II-3

SUBSTRATE HOLDER CAPABLE OF BEING COOLED (REF. 27;
NOTE THAT GROUND SHIELD CONFINES DISCHARGE
TO FACE OF HOLDER)

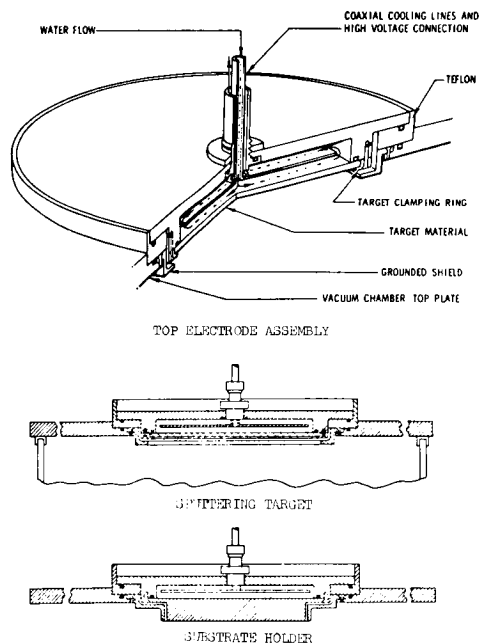


Figure II-4

SETUP FOR COATING A COMPLEX PART USING EVAPORATION FILAMENTS (REF. 51)

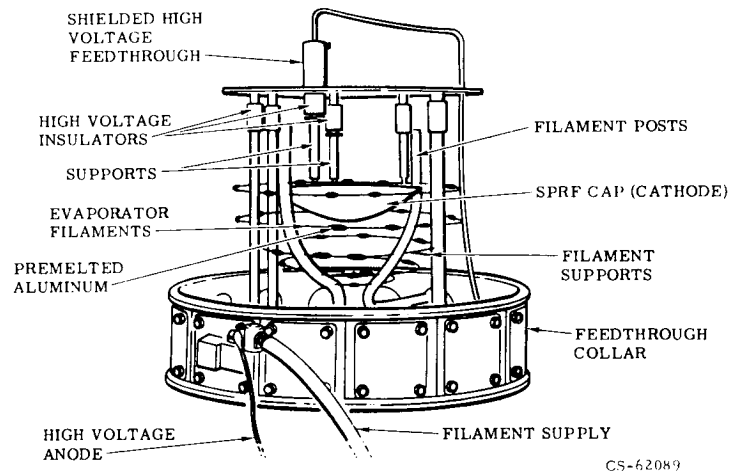


Figure II-5

VARIOUS TECHNIQUES FOR PROVIDING THE VAPOR TO BE DEPOSITED IN ION PLATING

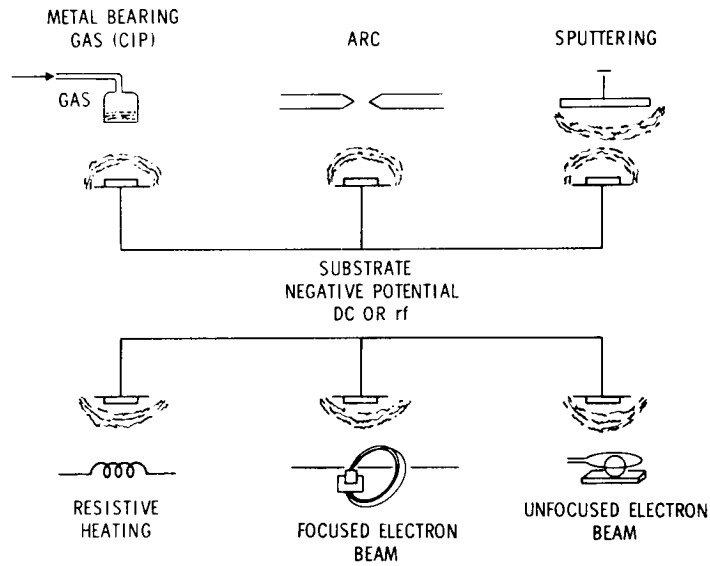


Figure II-6

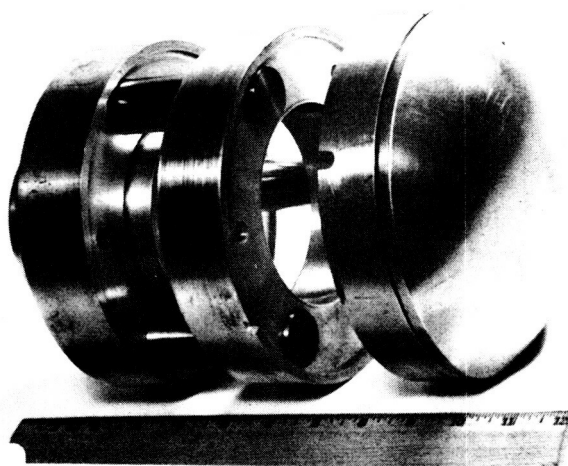
NICKEL-PLATED URANIUM SAFETY BLOCK AFTER BEING SUBJECTED
TO THE REACTOR ENVIRONMENT (REF. 51)



CS-62082

Figure II-7

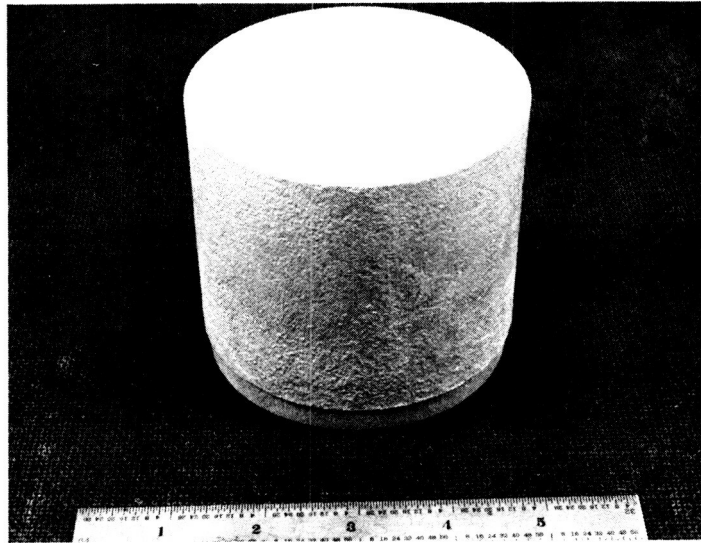
MOCKUP OF PULSE REACTOR URANIUM ASSEMBLY SHOWING PARTS PLATED (REF. 51)



CS-62083

Figure II-8

SAFETY BLOCK AFTER BEING PLATED WITH ALUMINUM (REF. 51)



CS-62081

Figure II-9

ELECTRON MICROPROBE TRACE OF URANIUM THAT HAD BEEN
ALUMINUM-ION PLATED AND DIFFUSED AT 600° C
FOR 70 MINUTES (REF. 10)

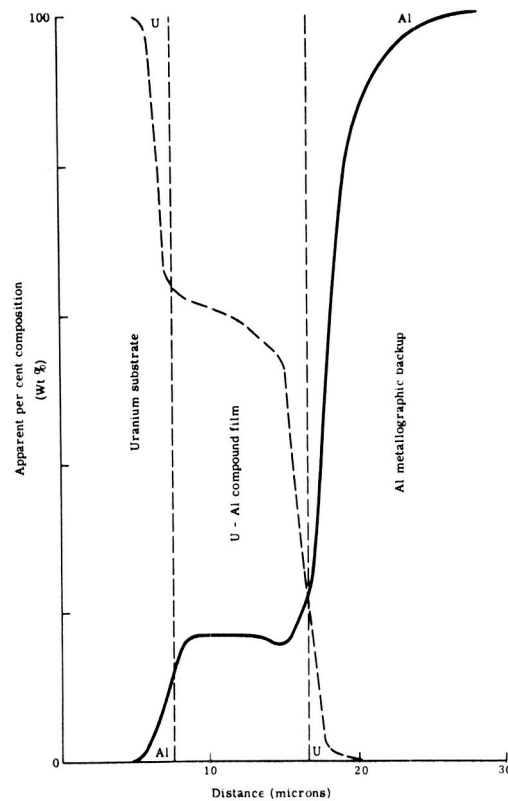
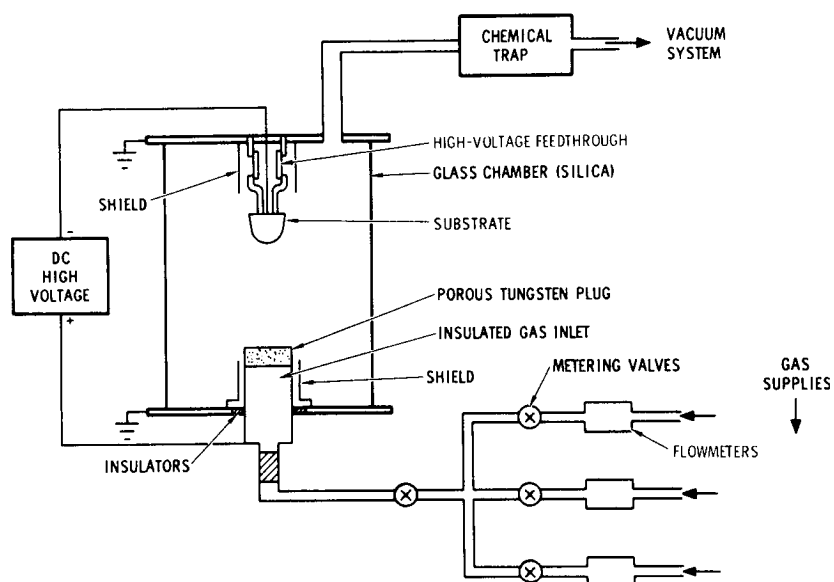


Figure II-10

CHEMICAL-ION PLATING APPARATUS FOR USING SEVERAL GASES TO DEPOSIT A COMPOUND
ON THE SURFACE OF THE SUBSTRATE (REFS. 31 AND 52)



CN-2187

Figure II-11

III. CHARACTERISTICS OF ION PLATED FILMS INCLUDING MECHANICAL PROPERTIES AND LUBRICATION

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When a coating is applied to a surface, the application method determines the bonding characteristics and adherence. These are reflected in the effectiveness and usefulness of the coating during its use. The degree of adherence is the most important factor since it is directly related to surface pretreatment, energetics of the coating material, the type and structure of interface formed, and the selection of materials (substrate and film). The method which shows the greatest potential to satisfy these requirements for tenacious adherence is ion plating.

On the basis of kinetic energy considerations, ion plating is a high energy or plasma deposition method. It differs from the other vacuum deposition methods in that the coating material is ionized and strikes the object to be plated in an ionized state. Basically, ion plating has a diode configuration. The object to be plated is the termination point for an electric field which exists between the evaporation source (anode) and the specimen (cathode). The evaporated material is injected into the argon plasma, ionized, and accelerated toward the specimen. The ionized atoms acquire high energies (3000 to 5000 eV) which depend on the potential directly applied across the electrodes. The specimen to be coated does not have to be a conductor.

Specimens which are insulators and organics can be coated when a slight modification is made. The versatility of the plating material used in this

process depends on the type of evaporation process selected. It should be noted that the film should retain the same chemical composition as the plating material. The simplest and fastest means of evaporating the material is by resistance heating. However, this technique is adequate only for the evaporation of elemental metals. Flash evaporation has been employed (ref. 1) where stoichiometric, low melting alloy films have been deposited; recently electron beam evaporation was introduced (ref. 2) to evaporate high temperature alloys and ceramics.

Ion plating has two distinct advantages: first, high kinetic energy of the ionized plating material, and second, high throwing power, which implies that complex, irregular geometrical objects can be plated (in cavities and around corners) with a uniform film.

The objective of this paper is to show by electron micrographs the films and interfaces formed during ion plating and to illustrate the performance of those films during friction and tensile tests. Since these films are deposited during high energy conditions, the film formation characteristics are strictly determined by the energetics. Friction tests conducted on ion plated films showed a longer wear life than conventionally applied films, and when the lubricant film was worn away no catastrophic failure occurred. This is due to the graded interface.

Ion plated films are now more widely used in lubrication for corrosion and oxidation protection and in decorating jewelry and novelty areas. Other less known areas where ion plated films can be used are also discussed in this paper.

ION PLATING APPARATUS AND PROCEDURE

The ion plating apparatus used in depositing metal films is shown photographically in figure III-1. This method is basically a diode system consisting of two electrodes. The specimen to be coated is the cathode of the high-voltage dc circuit, and the boat with the evaporant material is the anode. The construction details of the apparatus have previously been described (ref. 3).

The plating parameters used during ion plating are as follows: argon pressure, 20 microns; applied potential, 3 to 5 kilovolts; current density,

0.3 to 0.8 milliamperes per square centimeter. When a negative potential is applied to the specimen a glow discharge is formed. The most important region for practical ion plating is the dark region near the cathode (fig. III-2); in this region, known as the cathode dark space, the largest potential drop in the plasma. The significance of this cathode dark space is that within this region the ions are accelerated with the highest velocity toward the cathode. The width of the dark space can be expanded or contracted either by decreasing or increasing the pressure. As soon as the discharge is formed the ionized argon ions are accelerated toward the cathode and sputtering occurs. This sputter etching or cleaning of the surface is continued until the surface is cleaned of oxide layers and is free of skin effects of cold working which are produced with mechanical polishing. Generally, when sputtering begins, the initial current is high and some arcing may take place. While the surface is being cleaned by sputtering, the discharge current decreases until finally a constant value is reached. This constancy in discharge current is an indicator that the surface is cleaned. The main attribute of sputter etching is that one type of apparatus and procedure provides a simple means of etching a variety of metal surfaces. When the same sputter etching conditions are used, a good reproducibility of surface morphology is obtained. After the surface is cleaned by sputter etching (which depends on the type of the material), the boat is heated and the plating material evaporated. The evaporated metal atoms are injected into the plasma and ionized. The plasma is an ionized gas of argon for which the ionization potential of argon is 15.7 electron volts. The evaporated metals which are injected into the plasma have ionization potentials between 4 and 9.5 electron volts. The metal atoms in the argon plasma should therefore be easily ionized. A typical observable proof is the ionization of copper in argon plasma which produces a distinct color change during evaporation.

During ion plating the ionized metal ions accelerate toward the specimen (cathode) and arrive with a kinetic energy proportional to the potential difference between the specimen and the boat. Essentially, ion plating consists of two processes - sputtering (cleaning) and ion implantation. During ion plating two competing forces exist. While sputtering continues the ion implantation process is occurring to form a coating. The sputtering rate must be less than the deposition rate for a film to be deposited.

RESULTS AND DISCUSSION

Coating Complex Geometrical Surfaces

In ion plating the ionized metal atoms follow the electric lines of force to all points on the specimen surface. As a result, a uniform metal film can be deposited on any complex surface (in cavities and around corners) on specimens without rotation or movement. Figure III-3 illustrates the evaporation characteristics of the conventional vacuum deposition as compared to ion plating. For instance, components of ball bearings in figure III-4 can be ion plated with a uniform, adherent soft metal lubricant film such as gold, silver, lead, lead-tin, etc. The entire surface areas including the ball pockets of the cage are coated with the soft metal lubricant film. To further illustrate the effects of surface geometry, figure III-5 shows a threaded hollow cylinder, a gear, and a metal seal which were uniformly coated inside and outside with a gold film.

In this investigation the evaporation source is a resistance heated boat which is the simplest and quickest means for evaporating elemental metals on materials which are conductors. The same method can be also used when insulators must be coated by introducing only a simple modification (fig. III-1 insert). Since direct potentials cannot be applied to an insulator specimen, the insulator is placed inside a metal screen cage. This screen cage now acts as a cathode to which the potential is applied. Details of this modification were previously described (ref. 4). Consequently, when ion plating is used, any type of material (metals, ceramics, glass, or organics) can be coated with a metal film as shown in figure III-6.

As to selecting the coating material with respect to the evaporation source, it is important to select the appropriate source. When alloys or compounds have to be deposited, it should be remembered that the deposited film should retain its stoichiometry to the evaporant material. When low melting elemental metals have to be deposited, resistance heating is the quickest and most economic means of evaporation. When alloy and compound films have to be deposited, resistance heating cannot be used because of the thermal decomposition and dissociation. All alloys and compounds consist of components which have differences in vapor pressures. Because of these differences in vapor pressure, the components of the vapor vary

continuously during the evaporation time, and the resultant film formed is chemically inhomogeneous. To retain the stoichiometry of the film during the evaporation of alloys and compounds, flash evaporation can be used for evaporating low melting alloys and compounds and is referred to as ion plating with flash evaporation (ref. 1). Electron beam sources (ref. 2) are also used to evaporate high temperature materials such as stainless steels, ceramics, and glass.

High Energy Embedded Interface

In addition to the high throwing power available to coat the entire complex surface regardless of its geometry, the second advantageous feature associated with ion plating is the high energy ion flux of the depositing material. Film adherence is directly related to surface pretreatment, energetics of the depositing material, the type and structure of the interface formed, and the selection of substrate and film materials. Ion plating has two built-in features which are responsible for the exceptionally strong adherence. First, the surface of the specimen is sputter etched (cleaned) before plating and during plating, thus maintaining a clean, sputter etched surface until the first monolayer of the film is formed. Instead of using chemicals, the argon ions act as an "etching agent." The surface morphology during etching alters the state of the surface by creating a surface roughness on the atomic scale, thus activating the surface for stronger adherence. Second, the high velocity at which the ionized evaporant strikes the negatively charged surface determines the depth of penetration into the surface. The interface formed at these high potentials has a graded appearance with a gradual change in composition and lattice parameters. This concentration gradient in the composition contributes to the strong adherence of the film. The inherent stresses produced during film deposition are due to the differences in lattice parameters and the thermal expansion mismatch between the metal film and the substrate. These stresses are always minimized when a graded interface is formed. Therefore, peeling and blistering effects are not observed on ion plated films. When the potential difference between the specimen and the boat is 3 to 5 kilovolts, the average kinetic energy of the impinging metal ions are at about 3000 to 5000 electron volts.

In standard vapor deposition methods the depositing atoms have thermal energies of approximately 0.1 to 1 electron volt (ref. 5). Because of the high kinetic energy of the metal ions, the atoms strike the negatively charged specimen with high velocities, thus penetrating the surface. The depth of penetration depends on the mass of incident ion, mass of target ion, and energy of the incident ion. The mean penetration ranges and the range of distributions of many ions into a large number of crystals have been measured, and it is estimated that the mean ion range is 10 to 100 Å/keV (ref. 6).

Typical high energy embedded interfaces and their corresponding coatings were examined by electron microscopy as shown in figures III-7 to III-10. Figures III-7 and III-8 show a typical cross section of a tungsten surface ion plated with a nickel film. The tungsten surfaces in all cases before ion plating were electropolished. Three regions in the microstructure can be distinguished: nickel film, interface, and the tungsten substrate. Figure III-9 shows a typical cross section of a tungsten surface ion plated with gold. A graded interface can be also distinguished here. The interfaces formed here have a graded appearance which is in a way similar to a diffusion bonded interface. The microstructure of figure III-10 illustrates where titanium was ion plated on a tungsten surface. A titanium film about 2×10^5 Å thick was formed on the surface. The microstructure reveals that the film has a very dense packing, a strong particle-to-particle bonding, and does not show any porosity.

Frictional testing of ion plated films. - Soft metal films (Au, Ag, Pb, Pb-Sn, etc.) are used as lubricants to prevent seizure of moving or rotating machinery components. These soft metal lubricant films were deposited on metal parts by ion plating. Because of their exceptionally strong adherence the wear life of the components was extended. A typical illustration is shown and described with ion plated gold. Gold films about 2000 Å thick were ion plated on nickel and 52100 tool steel flat disks. Sliding friction tests in high vacuum were conducted where a 4.75-millimeter-radius hemisphere (rider) was loaded against the flat rotating disk coated with the gold film. Figure III-11 shows typical friction curves where friction tests were conducted on gold ion plated film and on gold film deposited by vapor deposition. The experimental friction parameters were kept constant in both cases. It is interesting to observe that when the rider wears through the ion plated film the coefficient of friction does not rise abruptly. The coefficient of friction

risers gradually, approaching the coefficient of friction for the bare metal. For the vapor deposited film the coefficient of friction increases very abruptly after the rider wears through the film. The comparison of the two films, especially the nature of the slope of the curves after the film is broken, confirms the presence of a graded interface in the ion plated film.

Tensile testing of ion plated films. - Another severe test to evaluate film adherence is the tensile test. A number of 2.54-centimeter gage length round nickel and 52100 tool steel specimens were machined. These specimens were ion plated with gold and tested in tensile tests. Figures III-12 and III-13 show the appearance of the tensile specimens before and after breaking. The broken nickel specimen in figure III-12 shows a "roughening effect" on the surface. These broken specimens indicate that during plastic flow the film deforms together with the bulk. No peeling or scaling effects of the film were observed. The total elongation for the nickel specimens was 38 percent and the reduction in area was 80 percent. The broken ion-plated 52100 tool steel specimen in figure III-13 had an elongation of 20.5 percent and a reduction in area of 56.2 percent, also, no separation of the film was observed here.

Another series of flat tensile specimens was machined from nickel and Inconel sheets, then fully annealed, and finally ion plated with extremely thin ($<1000 \text{ \AA}$) copper film. Considerable evidence exists to show that the mechanical properties and plastic deformation behavior of crystals can be markedly influenced by altering the state of the surface. The surface sensitive mechanical behavior is due to a structural alternation of the crystal lattice in the surface and subsurface regions and the subsequent effects on dislocation behavior in these regions (ref. 7). To observe the plastic deformation effects, the uncoated and ion plated specimens were tensile tested under identical conditions (at a constant strain rate and load). Load-elongation curves were autographically recorded for each test. Typical curves for nickel and Inconel specimens with and without a film are shown in figure III-14. There is a distinct difference between the plated and unplated specimens beyond the proportional limit. The plated specimens exhibit higher strength characteristics in the plastic region from 5 to 8 percent, such as increases in yield and tensile strengths. These load-elongation curves show that an extremely thin film can have a pronounced effect on the mechanical properties. It is believed that surface alloying was

responsible for the strengthening effects these films exhibited during plastic deformation. Studies are also presently being conducted to determine the ion plated film effect on the fatigue life during fatigue tests. Preliminary investigations indicate that these films increase the fatigue life.

Application of ion plating. - Because of the exceptionally strong adherence and the high throwing power to coat complex surfaces, ion plating is receiving an increasing level of acceptance in practically all areas where films may be needed. Ion plating has been used in lubrication where soft metal or alloy films are required to reduce wear. It should, for example, be feasible to ion plate chromium on the surfaces of M-50 bearings to improve the pitting-corrosion resistance. Surfaces which require protective coatings against atmospheric attacks like corrosion, oxidation, and sulfidation can be protected. These effects generally start at cracks and pores in the coating. The decorative field uses this method very effectively where precious metals are deposited on jewelry, glass bottles, or on any type of novelty. In the semiconductor field it can be used as a means of introducing impurities (doping). Just recently ion plating was used as a "welding method" to seal porosity and microcracks. This was demonstrated by sealing an ultrahigh vacuum flange with a glass window (fig. III-15) where a leak had developed. Any other welding method could not be used here since the metal-glass seal would be damaged.

In ion plating the normal solubility limits may be significantly exceeded, leading to the possibility of forming new second or intermediate phases. These new phases formed under these nonequilibrium conditions may form alloys which have not been recognized yet.

SUMMARY OF RESULTS

Ion plating has two distinct advantages over the conventional deposition methods. First, because of the high kinetic energy, the ionized plating material penetrates the surface when it strikes the specimen. Second, because of the high nondirectional throwing power the surfaces of complex geometrical objects can be plated without rotation. During ion plating a film is deposited on a surface cleaned by sputter etching, and due to the high velocity of the ionized evaporant material, a graded interface is formed. The type

and structure of the interface were determined by electron micrographs. The high degree of adherence was tested and evaluated in friction and tensile tests. When tensile tested the ion plated specimens reveal that during plastic deformation the film plastically flows with the bulk material without peeling or scaling. In addition, the load-elongation curves for the plated specimens exhibit strengthening effects in the plastic region of 5 to 8 percent, such as increases in yield and tensile strengths. The ion plated film has a surface strengthening effect which may be due to solid-solution alloying. Several new approaches of using ion plating are suggested, such as sealing porosity and microcracks in metal parts, pitting-corrosion resistance, and possibly forming new intermediate phases.

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ION PLATING CHAMBER

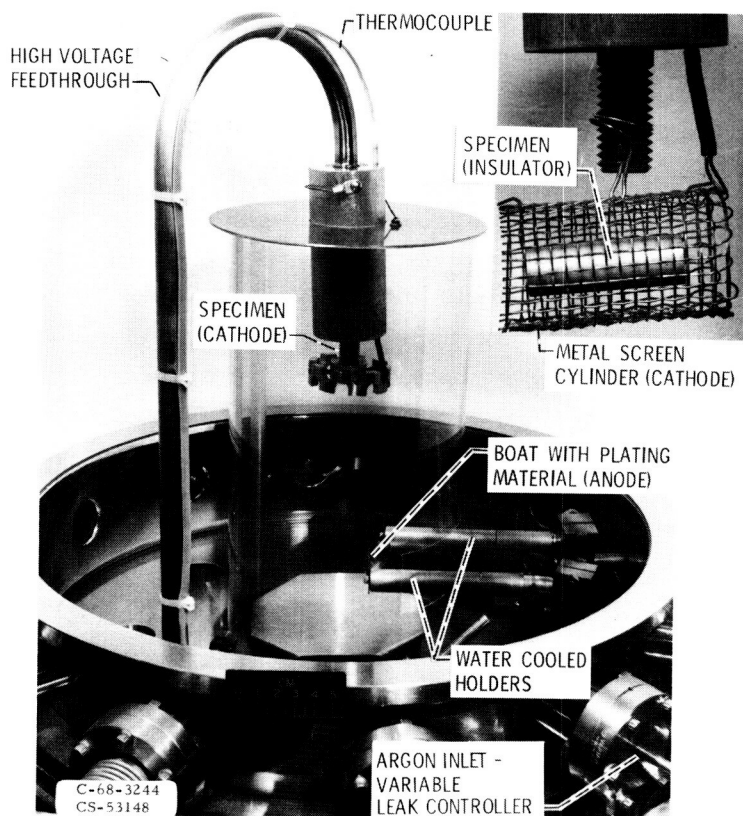


Figure III-1

GLOW DISCHARGE DURING ION PLATING

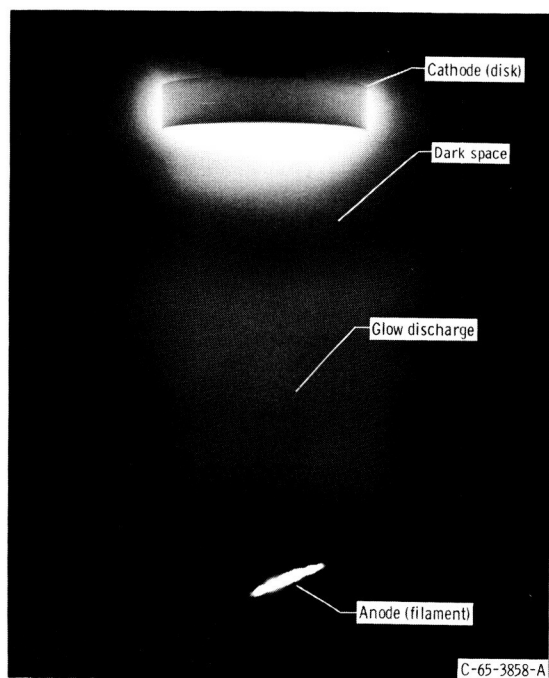


Figure III-2

COMPARISON OF CONVENTIONAL VACUUM DEPOSITION WITH
ION PLATING TECHNIQUES

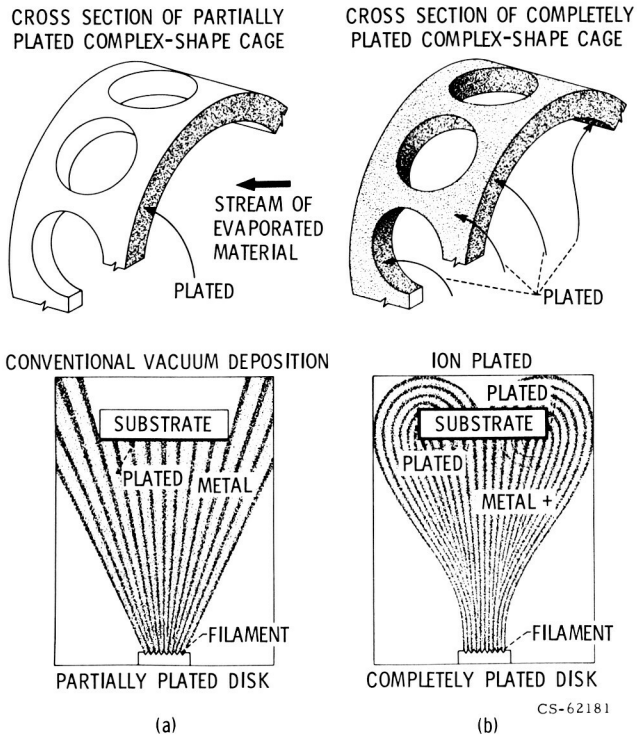


Figure III-3

GOLD ION PLATED AND UNPLATED BEARING ASSEMBLY

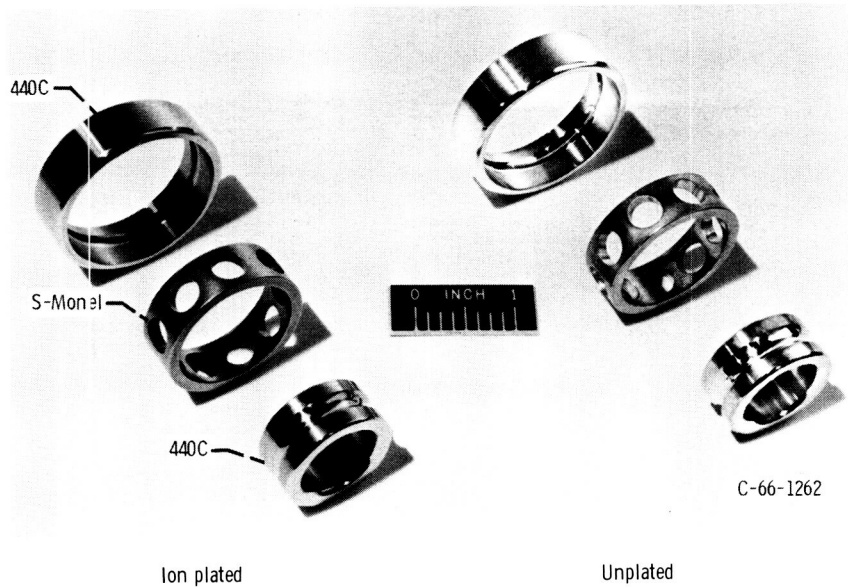
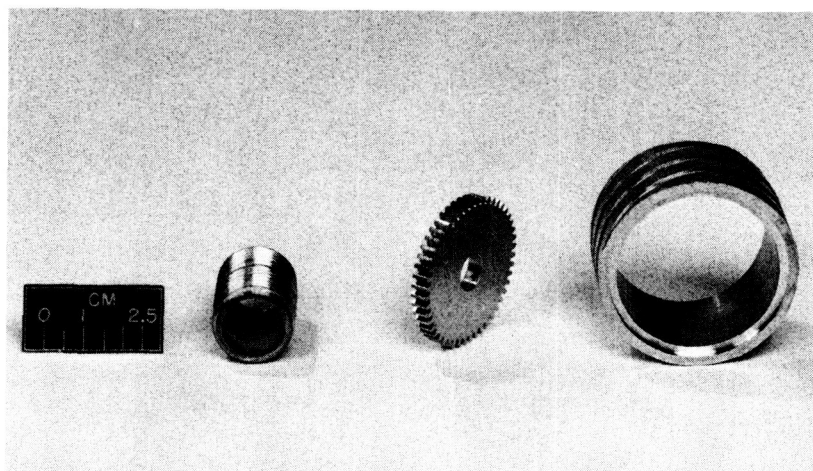


Figure III-4

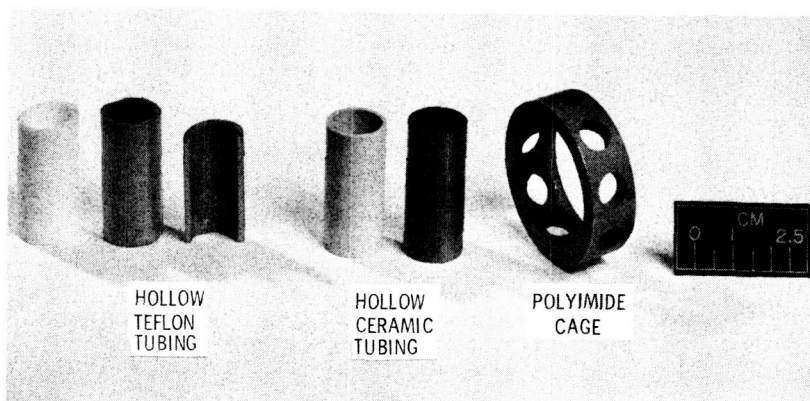
ION PLATED METAL OBJECTS OF COMPLEX GEOMETRIES



C-72-100
CS-62117

Figure III-5

INSULATORS COMPLETELY COATED WITH LEAD BY ION PLATING



C-69-3817
CS-53145

Figure III-6

ELECTRON MICROGRAPH OF CROSS SECTION OF NICKEL FILM APPLIED ON
TUNGSTEN SURFACE BY ION PLATING

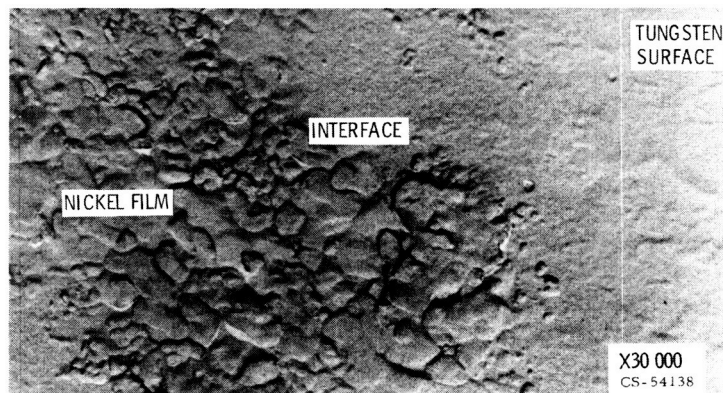


Figure III-7

ELECTRON MICROGRAPH OF CROSS SECTION OF NICKEL FILM APPLIED ON
TUNGSTEN SURFACE BY ION PLATING

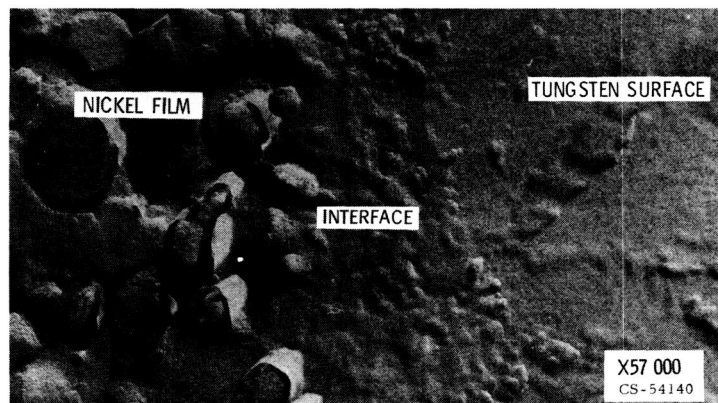


Figure III-8

ELECTRON MICROGRAPH OF CROSS SECTION OF GOLD FILM APPLIED
ON TUNGSTEN SURFACE BY ION PLATING

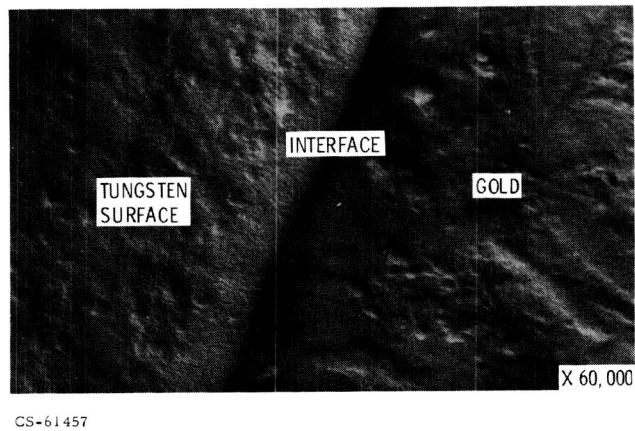


Figure III-9

ELECTRON MICROGRAPH OF CROSS SECTION OF TITANIUM FILM APPLIED
ON TUNGSTEN SURFACE BY ION PLATING

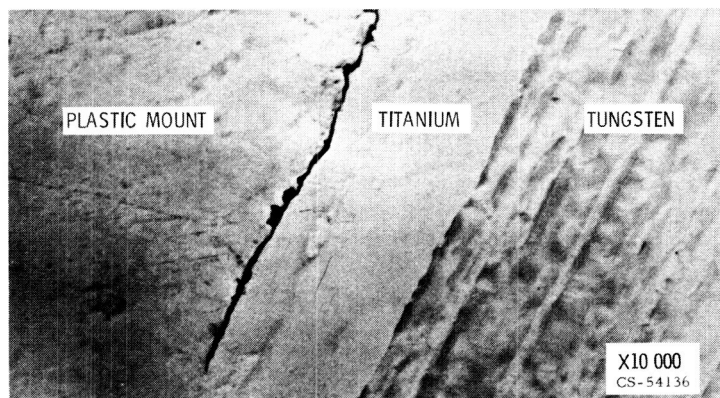


Figure III-10

COEFF OF FRICTION OF NIOBIUM SLIDING ON (Ni-Cr)
 ALLOY WITH GOLD DEPOSITED BY VAPOR DEPO-
 SITION, & ION PLATING ABOUT 2000 Å THICK
 (LOAD, 250 g; SPEED, 5 FT/MIN;
 AMBIENT TEMP, 10^{-11} TORR)

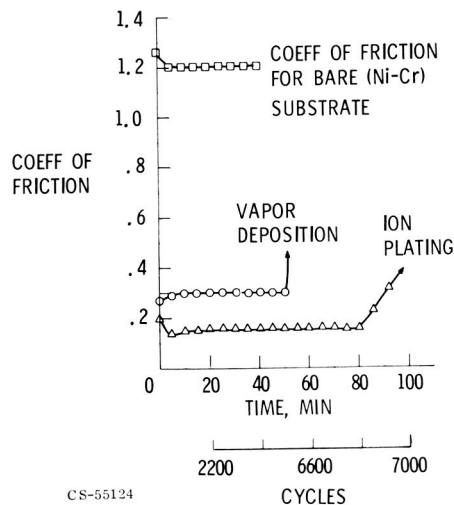


Figure III-11

COMPARISON OF UNCOATED AND GOLD ION PLATED NICKEL TENSILE
 SPECIMENS AFTER FRACTURE

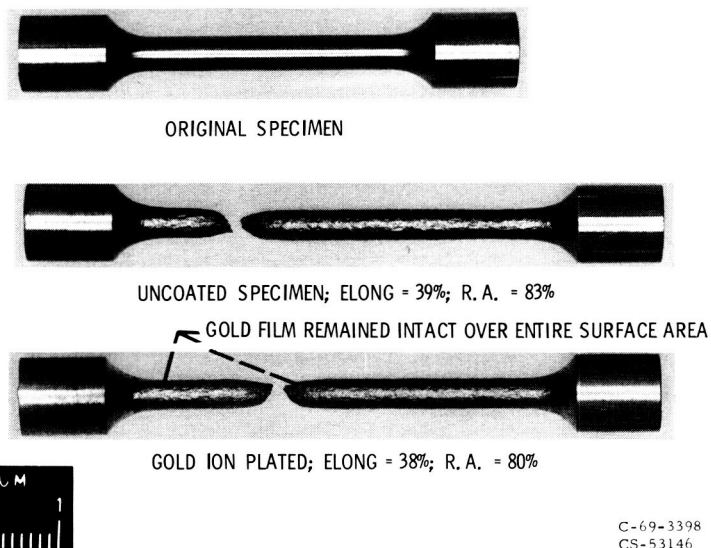


Figure III-12

COMPARISON OF UNCOATED AND GOLD ION PLATED TOOL STEEL 52100
TENSILE SPECIMENS AFTER FRACTURE

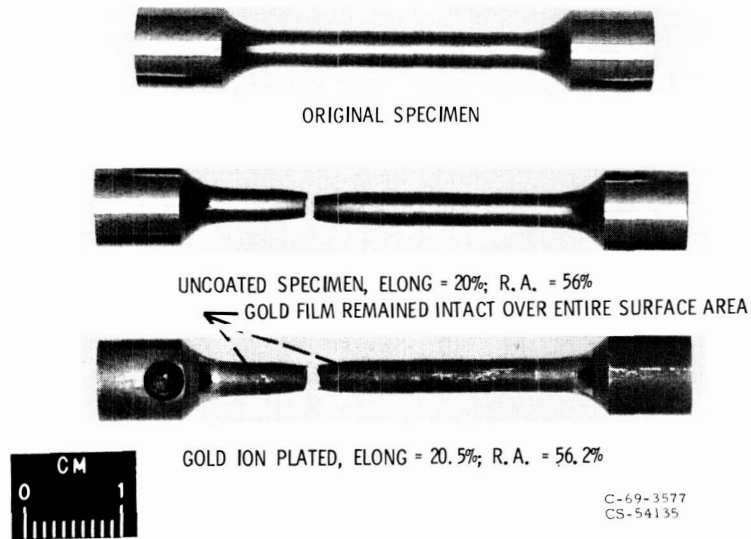


Figure III-13

LOAD ELONGATION CURVES DURING TENSILE TESTS

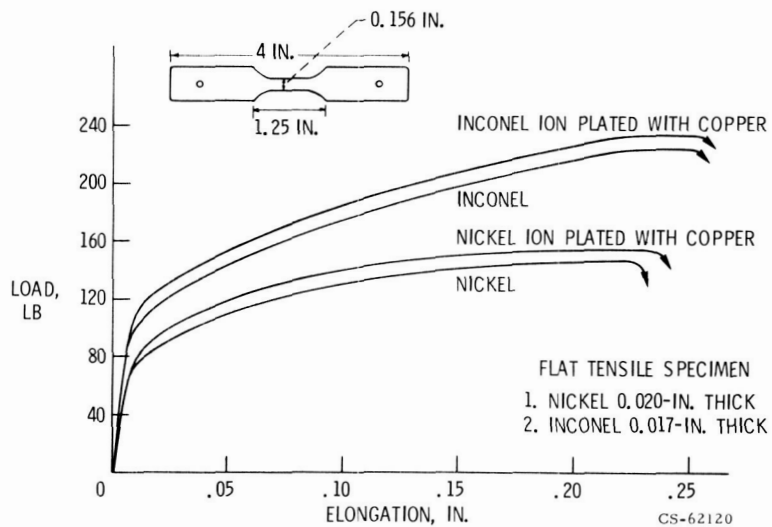


Figure III-14

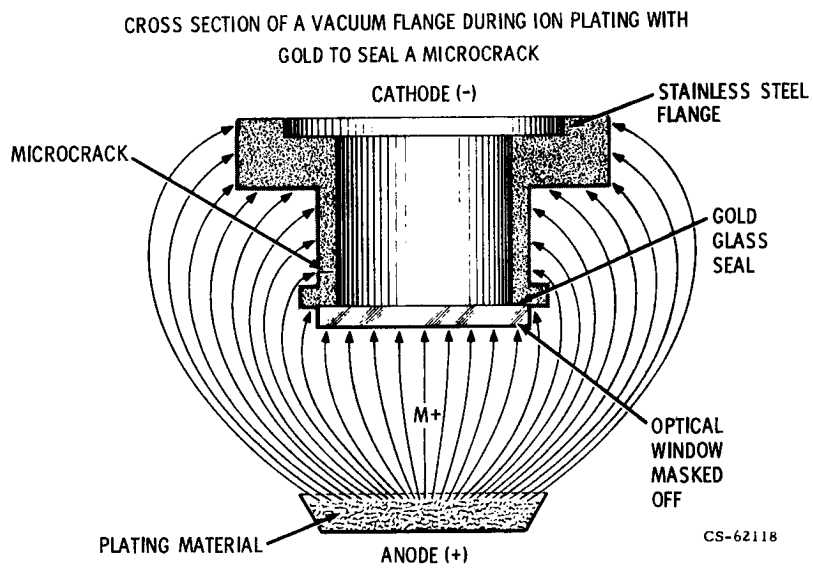


Figure III-15

IV. FUNDAMENTALS OF RF AND DC SPUTTERING

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Sputtering (i. e., the ejection of surface atoms from solids or liquids under ion bombardment) is of interest in many fields. Often sputtering is considered to be a nuisance, especially by those working with gas discharge or plasma devices, because it causes erosion of electrodes, deactivation of thermionic cathodes, blackening of tube walls, gas pressure changes (gettering), etc., and thus often limits the useful life of such devices. Others find sputtering beneficial, such as in the preparation of atomically clean surfaces, in etching, micromachining, and thinning, in gettering (as in the widely used getter-ion pumps), in sectioning for the determination of composition depth profiles with surface analysis methods, and in particular as a film deposition method. Here sputtering has to compete with many other deposition methods; among these are vacuum evaporation and ion plating, which are the main subjects of this conference.

Points to consider when evaluating the merits or shortcomings of sputter deposition are the following:

- (1) One can sputter clean the substrate by ion bombardment before starting the deposition.
- (2) Sputtering yields for different metals, alloys, or even insulators are not very different. Tantalum and tungsten sputtering yields, for instance, are only half that of aluminum. Thus, the compatibility makes sputtering attractive in sequential in situ deposition of different materials.
- (3) One can, if properly done, sputter deposit films of complicated materials such as stainless steel, Permalloy, or even Pyrex such that the

film has the same composition as the target material.

(4) The desired film thickness is simply achieved by determining the deposition rates under the specific geometric and discharge conditions and then by adjusting in subsequent runs the sputtering time correspondingly.

(5) One can sputter from large area targets or from targets of special shape. This is often advantageous with respect to film thickness uniformity or for coating substrates which have unusual shapes such as the inside of tubing, etc. Shadowing effects from dust particles on substrates which are often responsible for pin holes are less pronounced when the material arrives under many different impingement angles.

(6) No restrictions arise at the target from gravitational considerations. In fact, one often prefers downward sputtering because it simplifies substrate mounting.

(7) Targets can contain sufficient material to last for many deposition runs.

(8) With negative biasing of the substrate during film deposition, one can achieve preferential oxygen removal and obtain films of high purity.

(9) Controlled mixing of materials by sputtering from different targets usually causes no problems.

(10) If the discharge is operated at a gas pressure of less than 1 millitorr, many sputtered atoms arrive with their high kinetic ejection energy at the substrate. This is often beneficial with respect to film adherence. Epitaxial film growth on single crystal substrates can be achieved with sputtering at lower substrate temperatures than in vacuum evaporation.

(11) Sputtering in reactive gases or mixtures of noble and reactive gases (oxygen or nitrogen) can be used for tailoring compound films.

(12) In sputtering, one has so many (often very subtle, but important) parameters that it is difficult without inside knowledge to reproduce or imitate the products of a competitor.

(13) A serious disadvantage of sputtering is its low efficiency. Less than 5 percent of the kinetic energy of a bombarding ion goes into the kinetic energy of sputtered atoms. The other 95 percent appears mostly as heat in the target. As a consequence of this, one has to find a means for efficient target cooling if one wants to achieve high deposition rates. In insulator sputtering this can become a problem.

Scanning the current literature one finds a wide variety of thin film deposition tasks which investigators have tried to solve with sputtering. These tasks range from superconducting to cermet films (simultaneous sputtering of metals and insulators), from ferro- and piezoelectric to ferromagnetic films, from resistive, conductive, and insulating films used in hybrid microcircuits to protective, passivating, or ohmic contact films used in active devices, from coatings for better corrosion, abrasions, and wear resistance to solid lubricating films, from coatings of plastics for flexible circuitry or connectors to improving razor blades, from photo-emissive films to coatings with certain desired optical or radiative properties, etc.

Typical manufacturing areas in which sputtering is now well established are tantalum films for hybrid circuits, platinum-titanium - platinum-gold films in beam lead technology, passivating silicon dioxide films in memory devices, and chromium or chromium-platinum coatings on razor blades.

The basic physics in the sputtering process is now fairly well understood, and it is hardly necessary to repeat here what has been described in detail in many survey articles. One knows now that important parameters which determine yields (atoms per ion), thresholds (minimum kinetic energy of ions for sputtering to become noticeable), and angular distribution of ejected atoms (atoms, ions, or clusters) are primarily the masses of ions and target atoms, the outer electronic configurations of the collision partners, the angle of incidence and the kinetic energy of the impinging ions, the crystal structure and crystal orientation of the target material, and the binding energy of target atoms (heat of sublimation). If the mean free path of the sputtered atoms is small in comparison to the distance between the target and substrate (which is usually the case at pressures above several microns), many additional effects resulting from collisions between gas atoms, ions, sputtered particles, and electrons come into play. Thus, normal glow discharges which operate only at fairly high gas pressures are not well suited for basic studies, although they are widely used for film deposition.

The main progress in understanding the basic process in sputtering has come from studies in low gas pressure triode systems where the plasma is

formed independently as the positive column of a discharge maintained between a thermionic cathode and an anode. The target is inserted in this plasma as a separate negative electrode. By operating at gas pressures where the mean free path of ions and sputtered atoms becomes comparable or larger than the ion accelerating region or the tube dimensions, one eliminates many complications such as the diffusion of sputtered material back to the target, poorly defined energies and angles of incidence of the bombarding ions, charge exchange effects in the ion accelerating region, and ionization of the sputtered neutral atoms which travel with high ejection speeds from target to substrate through the plasma.

A complete understanding of film formation requires finally an analysis of the nucleation and growth conditions of the film at the substrate. Here surface migration and agglomeration, presence or formation of nucleation centers, the energy of the impinging atoms, the cleanliness of the substrate surfaces and their temperatures during deposition, the arrival rate of sputtered atoms (in particular, in comparison to the arrival rate of impurity atoms from the gas), the sticking coefficients of various species, the substrate ion bombardment (biasing), substrate bombardment by electrons or negative ions ejected from the target, etc. are all possible parameters which may have a pronounced influence on certain film properties. The large variety of parameters which enter require knowledge and good judgement in such areas as collision phenomena, plasma surface interactions, vacuum and plasma physics, material science, nucleation, growth, properties of films, etc.

Before radiofrequency (rf) sputtering was invented it was considered impossible to sputter insulators because one could not apply the ion accelerating potential to an insulator surface. An insulator surface in a plasma charges somewhat negative with respect to plasma potential just as a floating electrode does. This results from the fact that more mobile electrons than sluggish ions are striking the surface of a target per second. The required net current of zero at an insulator surface can only be achieved if some of the electrons are repelled, and the electrode accomplishes this by becoming more negative.

With rf potentials one has a possibility to enhance this negative charging. An ac potential applied to an electrode in a plasma draws a much

larger electron than ion current and acts therefore like a rectifier. If one arranges a large capacitor in series with a metal electrode in a plasma and applies an ac voltage, the electrode accomplishes the required net current of zero by shortening the electron receiving part of the period, i.e., charging up more negatively. The average dc voltage at the capacitor (which now becomes negative at the target side) is then nearly as large as the ac voltage amplitude. The dielectric in the series capacitor can consist of an insulator which separates the metal electrode from the plasma. This insulator surface then becomes negatively charged and is subject to sputtering. If one wants to accommodate larger amounts of insulator material to be sputtered, one ends up with a very small capacitance which would with ac not be sufficient for maintaining the negative voltage over nearly the whole period. Thus, one has to go to higher frequencies and this is the basis of rf sputtering. In many sputtering systems one uses the rf for an additional purpose, namely the creation of the plasma. Efficient plasma generation requires frequencies above 10 megacycles, and the resulting rf diode sputtering systems operate usually at the allowed band of 13.65 megacycles. Radiofrequency insulator sputtering has contributed tremendously to the popularity of sputtering in recent years, and equipment is now commercially available in many variations for sputtering in a plane parallel or cylindrical or even semishperical fashion.

Some of our own efforts at present are directed toward the use of new research tools such as Auger electron spectroscopy and secondary electron microscopy for studying certain aspects of sputtering. Auger electron spectroscopy is an ideal surface analysis method for in situ study of composition changes at ion bombarded alloy or compound targets or at sputter deposited films. One can readily observe with Auger, for instance, how the lower sputtering yield nickel becomes enriched at the target surface of a constantan (55 Cu - 45 Ni) target or how negative substrate biasing changes the composition in the sputter deposited film such that it becomes very deficient in copper. Figure IV-1 shows a cross section of our apparatus for in situ sputter cleaning, sputter deposition, and Auger analysis. In the sputtering mode, the system is flooded to 1 micron argon pressure; for analysis, it is pumped to the 10^{-9} torr region. The samples are mounted at a manipulator and can be rotated from the triode sputtering

chamber to the Auger analyzer. Figure IV-2 shows a typical Auger spectrum, such as that of a silicon wafer before and after sputter cleaning. Sputter cleaning has removed most impurities but has added imbedded argon. A puzzling phenomenon was discovered recently with Auger electron spectroscopy - namely, that certain atom species are very difficult to sputter from certain other substrate materials. For instance, 200 electron volt Ar^+ ions remove the last traces of molybdenum atoms which were deposited on an aluminum surface with a yield which is more than three orders of magnitude lower than the bulk molybdenum yield. Figure IV-3 shows that deposition of 12 monolayers of molybdenum on various metals leads to quite different initial coverages (agglomeration) and different removal rates. The low removal rate of molybdenum from aluminum is responsible for the formation of cones at an aluminum target which is seeded with minute amounts of molybdenum during sputtering. The molybdenum atoms surface migrate together to form little islands which then protect the underlying material from sputtering and leave the cones behind. These cones are shown in the photomicrograph of figure IV-4. A striking example of the role of small amounts of impurities in such cone formation was obtained when 98 and 99.999 percent aluminum were sputtered side by side under the same conditions. The pure aluminum shows only etch features which are characteristic of crystallite orientation and grain boundaries (furrows), while the impure target material is covered with closely spaced cones. The contrast between the two surfaces is shown in figure IV-5.

The scanning electron microscope turns out to be an ideal tool for examining and documenting cone formations and other target sputter etch surface features, and it also gives a wealth of information on many details in the deposition process. (For example, figure IV-6 shows cones on a gold target caused by chromium deposition.) Tungsten tips are being used in these studies as substrates, and our goal is to study characteristic differences between sputter and evaporation deposition films. By performing both operations in the same plasma environment, one can find characteristic differences which arise as a result of the widely different kinetic energy of the deposited atoms.

One recent discovery concerns the growth of genuine whiskers of cop-

per, gold, silver, and nickel when these materials are sputter deposited at a slow rate onto tungsten wires which are kept at an anode potential. Some of these whiskers can be seen in figures IV-8 to IV-10.

Another effort is directed toward the collection of data of sputtering yields and thresholds of insulators, a field in which reliable data are still lacking.

SCHEMATIC OF SYSTEM FOR IN SITU SPUTTERING AND AUGER ANALYSIS STUDIES

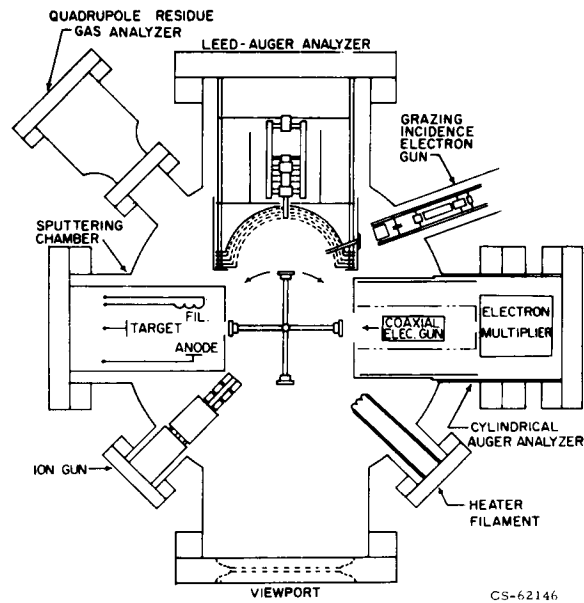


Figure IV-1

AUGER SPECTRUM OF SILICON WAFER BEFORE AND AFTER SPUTTER CLEANING

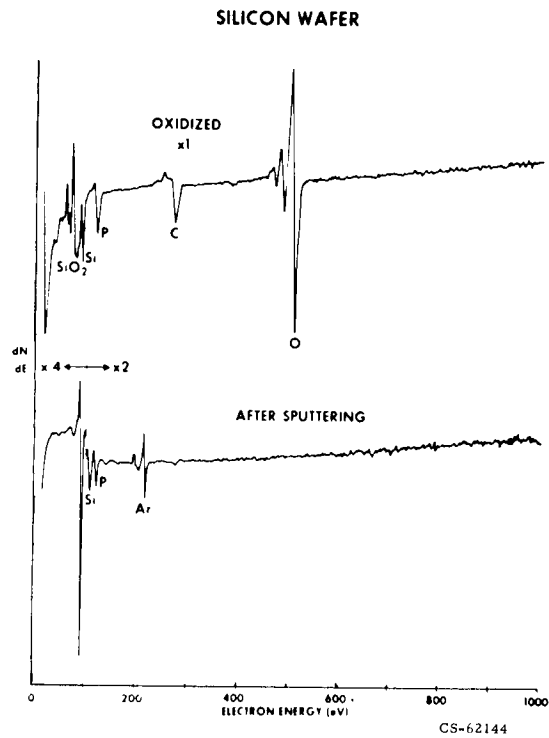


Figure IV-2

SPUTTER DEPOSITION AND REMOVAL OF MOLYBDENUM FROM VARIOUS METALS

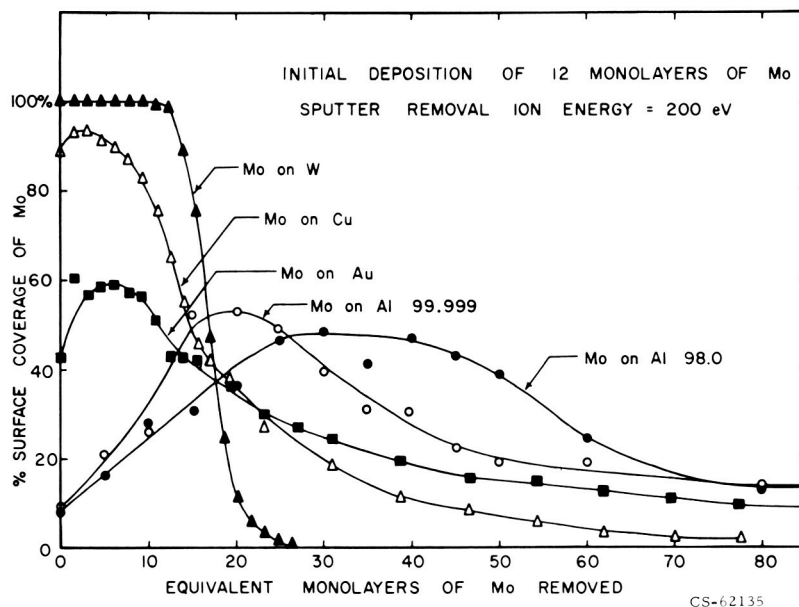


Figure IV-3

CONE FORMATION ON SPUTTERED ALUMINUM SURFACE (98 PERCENT PURITY)

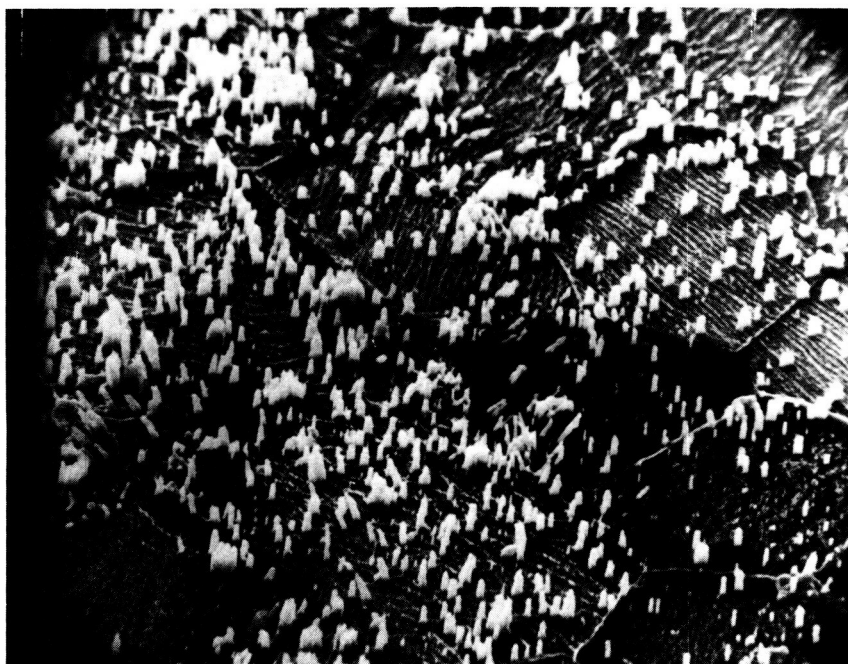


Figure IV-4

CS-62148

DIFFERENCE BETWEEN HIGH AND LOW PURITY SPUTTERED ALUMINUM TARGET

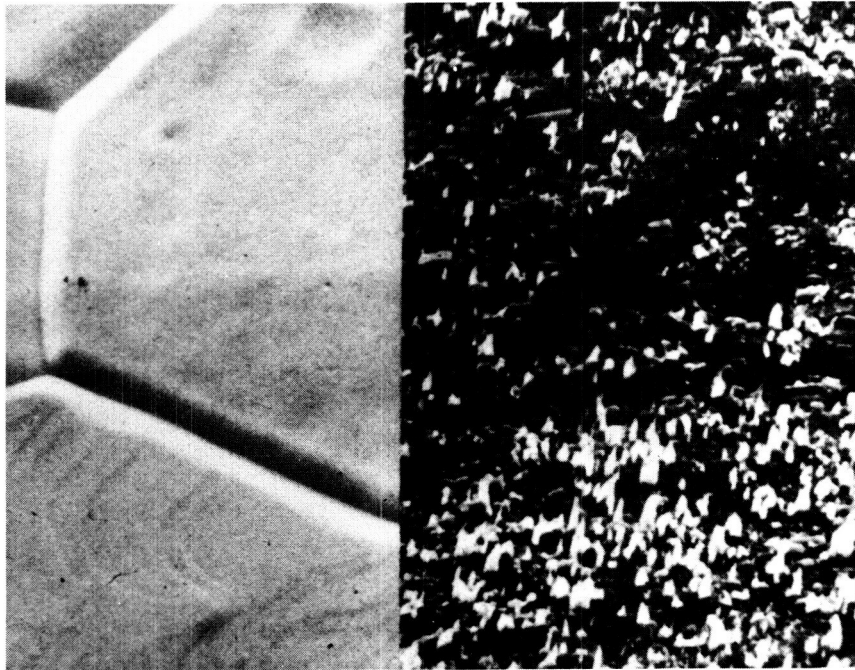


Figure IV-5

CS-62137

CONE FORMATION ON GOLD TARGET EXPOSED TO CHROMIUM DEPOSITION

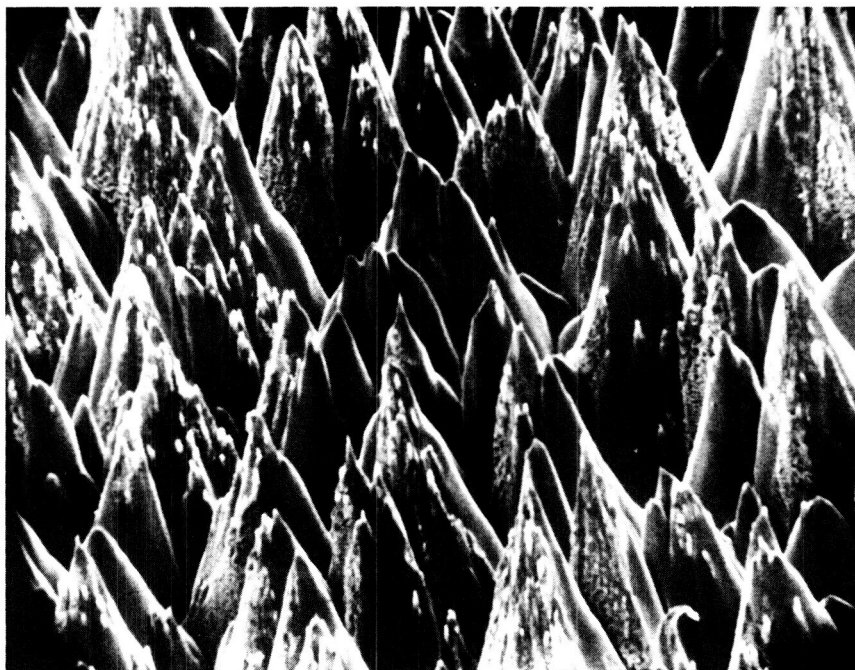


Figure IV-6

CS-62145

COPPER SPUTTERED ONTO TUNGSTEN WIRE SHOWING WHISKER GROWTH

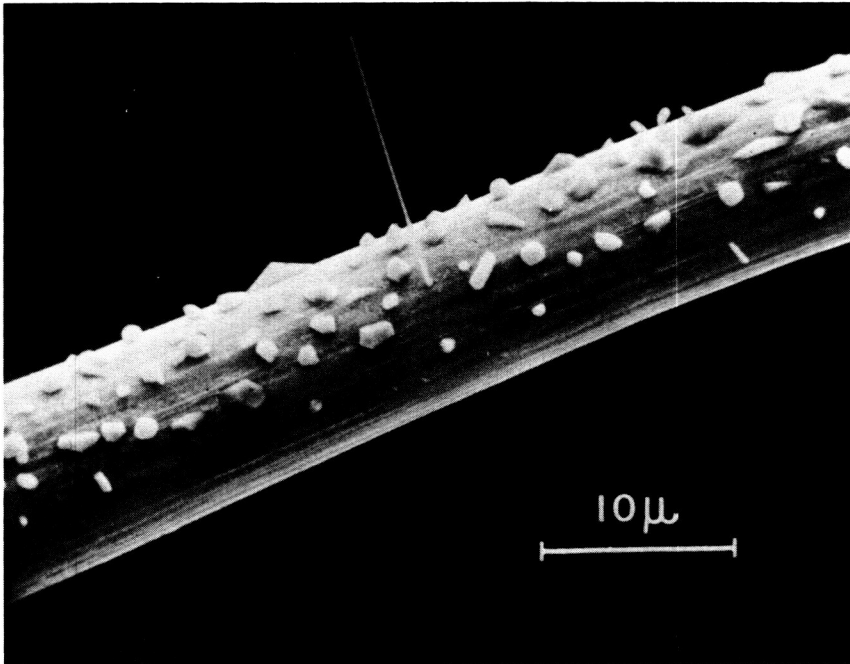


Figure IV-7

CS-62136

COPPER SPUTTERED ONTO TUNGSTEN WIRE SHOWING WHISKER GROWTH

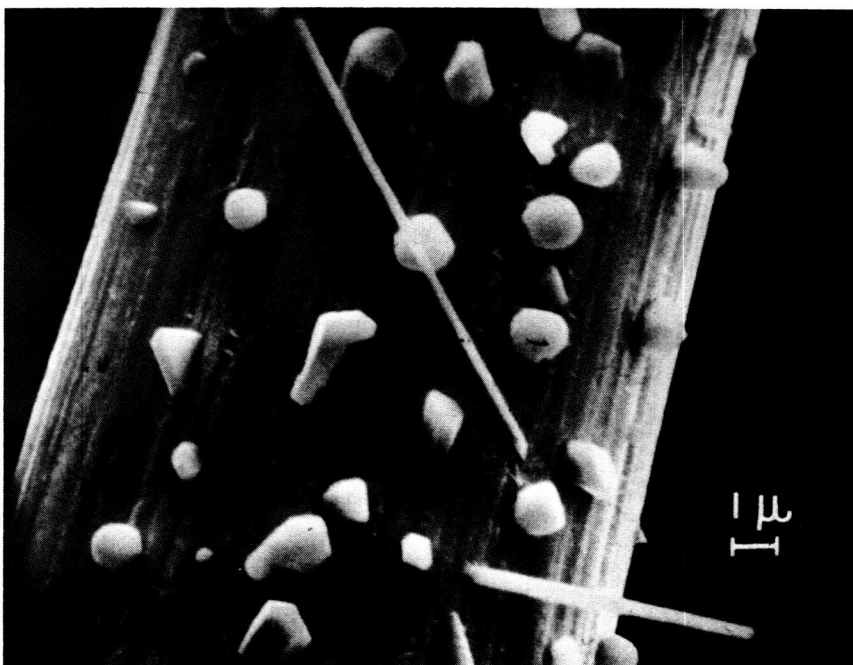


Figure IV-8

CS-62141

COPPER DEPOSITED ON TUNGSTEN TIP WITH WHISKER GROWTH

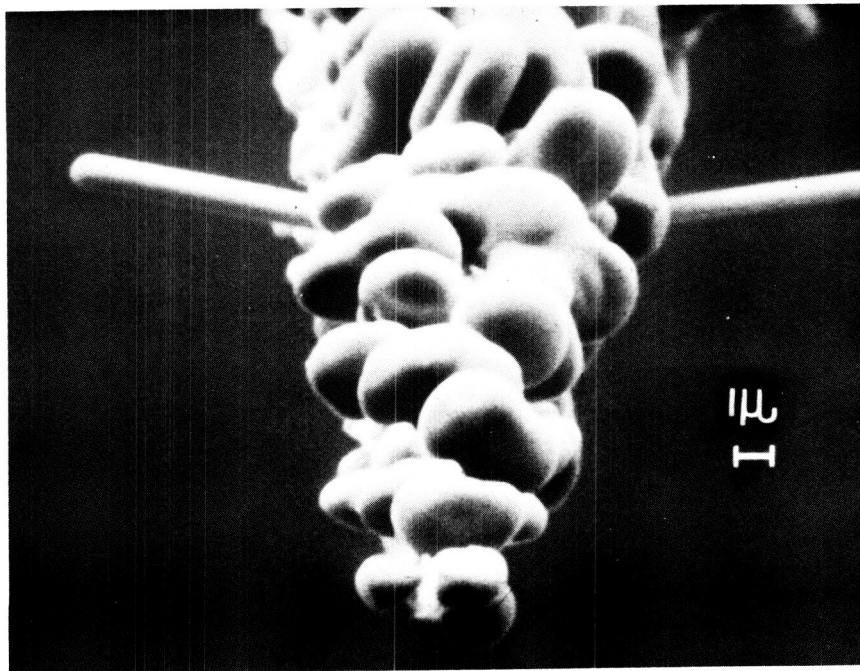


Figure IV-9

CS-62147

COPPER WHISKER WHICH CHANGED DIAMETER DURING GROWTH

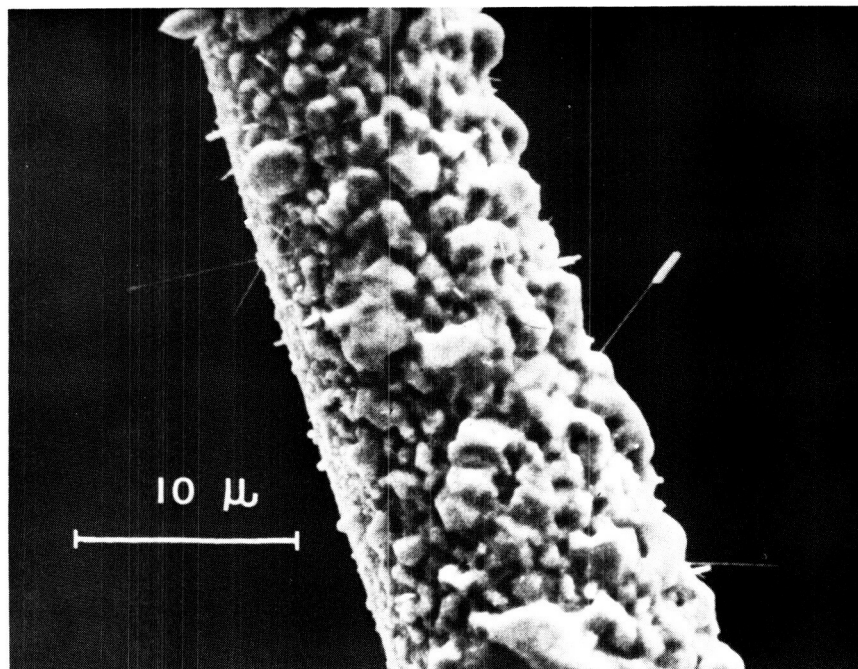


Figure IV-10

CS-62140

V. USE OF SPUTTERING FOR DEPOSITION OF SOLID FILM LUBRICANTS

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The deposition of thin films on surfaces by sputtering, both rf and dc, may have practical application in many areas (refs. 1 to 4). Sputtering is unique in that it allows for the deposition of a wide variety of materials on an even wider variety of substrates: Metals, alloys, ceramics, semiconductors, and plastics can all be deposited in the same apparatus by sputtering. Substrates can cover the gamut of materials from metals to paper. Films deposited by this technique are dense (pore free), cover the surface fairly uniformly, and are very tenacious.

The fact that sputtered films can be applied to a wide spectrum of surfaces with a resulting dense and strongly adherent nature makes such coatings potentially useful in corrosion protection, decorative applications, and lubrication. The objective of this paper is to discuss one area of application of sputtered film, namely, that of lubrication.

There are many solids that are used to lubricate material surfaces. These include soft metals such as lead, silver, gold, tin, zinc, and cadmium; inorganic compounds with layer latticed structures such as molybdenum disulfide and tungsten disulfide; and polymers such as Teflon, nylon, and polyimide. While all of these solids have been successfully sputtered, this presentation is restricted to a discussion of two of these materials, namely, molybdenum disulfide (MoS_2) and Teflon (PTFE). Both the deposition and lubricating properties of these materials are discussed. Films applied by sputtering are compared to films applied by more conventionally used techniques.

APPARATUS

Radiofrequency Sputtering System with dc Bias

The sputtering apparatus used for the deposition of lubricant films has an rf diode mode with a superimposed dc bias. The apparatus is shown schematically in figure V-1(a) and photographically while operating in figure V-1(b). The apparatus consists of a water-cooled metal electrode to which the MoS_2 or Teflon target material is bonded. The bonded target is a circular disk 0.63 centimeter thick and 12.7 centimeters in diameter. The system consists of three electrodes: (1) the target to which the rf potential is applied, (2) the specimen which is at a negative dc potential, and (3) the metal screen which is at a positive dc potential. The system provides the capability of substrate cleaning or etching followed by rf sputter deposition or simultaneous etching and sputter deposition.

In order to clean the specimen by etching, a negative potential (2 to 5 kV) is applied, with respect to the screen, to the specimen. A glow discharge is established in the presence of the sputtering gas (usually argon), and etching of the surface begins. When the surface is clean the rf power source (1-kW capacity) to the target is energized and film deposition by rf sputtering of the target occurs. While rf sputter deposition is occurring, the dc voltage applied for cleaning can be turned off or reduced appreciably such that the rf sputtering deposition rate exceeds the dc cleaning or material removal rate. A shutter is placed between the target and the specimen during dc sputter etching to prevent target contamination.

Friction Apparatus

The lubricant films applied by sputter deposition were evaluated, with respect to their lubricating properties, in a vacuum friction and wear apparatus. The apparatus consisted basically of a hemispherical rider sliding against a rotating flat. The rider was loaded against the rotating flat. With the use of a bellows and gimbal assembly the friction force between the specimens was transmitted to a strain gage measuring device for monitoring. Friction experiments were conducted at various speeds from 40 to 80 rpm

using loads of 250 to 1000 grams in a vacuum. The friction coefficient, wear to the rider, and number of repeated cycles over the same surface to film failure were used as criteria for determining the effectiveness of the film as a lubricant.

Sputtering Procedure for Deposition of Lubricant Films

The first step in the sputtering process is to evacuate the vacuum system to a pressure of 10^{-6} torr. The system is then bled to a pressure of 15 to 17 microns by the introduction of argon gas. A voltage of 2 to 5 kilovolts is applied to the specimen to be coated which establishes a glow discharge. This results in sputter etching of the specimen surface. After the specimen surface has been satisfactorily cleaned by sputter etching, the dc voltage is turned off and rf power is applied to the target. The necessary power is monitored by power readout meters.

With MoS_2 films, for example, the following rf sputtering parameters were used: rf frequency, 7 megahertz; argon pressure, 15 to 17 microns; power input, 400 watts; reflective power, about 2 watts; dc input for etching, 500 volts; target voltage (ac), 1.2 to 1.3 kilovolts; target to specimen distance, 2.54 centimeters. The use of these parameters resulted in a sputtering rate of about 150 angstroms per minute. The specimen temperature when the aforementioned power levels were used was 90°C .

RESULTS AND DISCUSSION

Molybdenum Disulfide Film

Films of MoS_2 were successfully sputtered onto a variety of substrate materials. The resulting film appeared to have all of the physical characteristics of the parent MoS_2 target. To ensure that the resulting film was in fact the same, the film was analyzed by electron microscopy, electron diffraction, and routine wet chemical analysis. Electron dark field transmission micrographs (at $\times 154\,000$) were taken of MoS_2 films on various substrates. These micrographs were essentially the same in appearance. A

typical one is shown in figure V-2. The film has a continuous and structureless appearance. There is no evidence of grains or grain boundaries. Additional micrographs were obtained at magnifications to $\times 500\,000$ in order to resolve particle or crystallite size. Individual particles or crystallites could not be resolved indicating that the individual crystallites must be less than 30 \AA in diameter.

The transmission electron microscopy did not reveal any discontinuities in the film. It also did not reveal any pinholes greater than 30 \AA in size. If they were present they would have appeared in the micrographs. Their absence indicates a very dense film. This characteristic of the sputtering process (which is to provide dense films) can be very beneficial where films are applied to provide corrosion protection to surfaces. Pinholes are a frequent problem with more conventional plating techniques such as electrodeposition.

Electron diffraction patterns were obtained from sputtered MoS_2 films on substrates such as nickel, glass, and mica. The diffraction patterns were essentially the same and are represented by the typical pattern of figure V-3. The very broad and diffuse ring obtained indicates a lack of crystallinity in the film. They may simply mean that the crystallite size was so small that it could not be resolved.

A chemical analysis was performed on MoS_2 films deposited by both rf and dc sputtering to determine if there was any difference between the chemistry of the standard MoS_2 target material and the resulting sputter deposited MoS_2 film. The results from such an analysis are presented in table V-1. An examination of table V-1 indicates that (1) the dc and rf sputtered films had nearly the same composition, (2) the sputtered films had approximately the same composition as the starting or target material, and (3) the composition did not vary greatly from coating to coating using the same sputtering technique.

The use of sputtering for the deposition of elements such as metals presents no need for analysis. With compounds, however, the problem of possible bond scission in the compound as a result of the energies associated with the sputtering process exists. Should this occur, we must ask whether the resulting compound fragments recombine on the substrate to be coated to the initial starting material composition or is some new compound formed. Furthermore, with a material such as MoS_2 , where one constituent (sulfur)

TABLE V-1. - CHEMICAL COMPOSITION OF DC AND RF

SPUTTERED MoS₂ FILMS

Experi- ment	Composition of original MoS ₂ , wt. %	Composition of dc sputtered film, wt. % (a)	Composition of rf sputtered film, wt. % (b)
1	Mo 58.60 S 39.44 Fe .12	Mo 58.23 S 38.90 Fe .11	Mo 58.8 S 40.3
2	Mo 58.90 S 39.44 Fe .12	Mo 58.55 S 38.65 Fe .10	Mo 60.3 S 38.6
3	--- ----- --- -----	--- ----- --- -----	Mo 61.10 S 39.20

^aExperimental condition: Voltage, 3.5 kV; current, 20 mA;
argon pressure, 20 μ .

^bExperimental condition: Power input, 400 W; argon pressure, 15 μ .

is volatile in vacuum, some of the volatile constituent may be lost in the transport process from the target to the specimen substrate. This could result in a film deficient in one compound constituent.

The analytical results obtained with sputtered MoS₂ films indicate that the molybdenum to sulfur ratios are not altered by the sputtering process. Furthermore, the physical appearance, color, and density are those of unsputtered MoS₂. As will be seen in the discussion of lubrication results, the friction properties of sputtered and unsputtered MoS₂ are essentially the same.

One of the requirements for any coating process to be very practical in the application of lubricant film is that it must be able to apply the film to complex surfaces. The reason for this requirement is that most surfaces requiring lubrication are not simple flats but have many corners, edges, and

are frequently circular in nature. Examples are bearing retainers, gears (teeth), and seals. This requirement can be met by sputtering.

If during the sputtering process the specimen to be coated is placed about $7\frac{1}{2}$ centimeters from the target, is floating, and all of its sides are exposed to the plasma sheath, it can be coated on all surfaces. This is demonstrated by the photographs in figure V-4 where an rf sputter coating of MoS_2 was applied to three elements of a ball bearing - the inner race, the cage, and the outer race. All surfaces of each of the three components were coated (except support points). The same three ball bearing elements uncoated are also shown in figure V-4. Thus, sputtering can be used to apply lubricant films to the complex surfaces encountered in practical lubrication systems.

A very important requirement to the application of coatings in general is that the coating material adhere strongly to the surface to be coated. This is true whether the coating is applied for corrosion protection, decorative, or lubrication purposes, but it is especially true where the film is for lubrication applications. It is very difficult to measure quantitatively the adhesion of thin films to substrates. A qualitative indication of film adherence, however, can be obtained from the tensile fracture of tensile specimens. When these are pulled to fracture with the surface film remaining intact it is evidence for good adhesion.

Nickel and Inconel tensile specimens were coated with rf sputtered MoS_2 films and the specimens were pulled to fracture. Photographs of coated and uncoated specimens are presented in figure V-5. With the nickel specimens and 38.5-percent elongation, the MoS_2 remained intact to fracture of the nickel. The surface of the tensile specimen became roughened because of plastic flow of the nickel, and yet the MoS_2 did not spall or flake off the surface. If this same experiment were conducted with conventionally applied MoS_2 films the coatings would spall off of the surface during elongation. With the sputtered film, the film remained on the surface even into the necking region of the specimen. Similar results were obtained with Inconel as shown in figure V-5.

Sliding friction experiments with films applied by rf sputtering have indicated that extremely thin films can provide very effective boundary lubrication. The effect of a 2000 \AA MoS_2 film on the friction coefficient for metals in sliding contact is shown in figure V-6. For the bare metals in

sliding contact the friction coefficient exceeded 1.0 and was initially nearly 2.0. With 2000 Å of MoS₂ on the surface of the flat specimen the friction was 0.08 indicating effective boundary lubrication. This friction coefficient is the same as obtained with commercially available MoS₂ coatings. It is comparable to that obtained with oils and greases.

With solid film lubricants it is not only important that they reduce friction and wear but that they are generally required to have a long wear life; that is, the film must be able to withstand repeated rubbing or sliding passes over the same surface. The data of figure V-7 represent the friction behavior of a bearing steel coated with a sputtered MoS₂ film. The initial friction coefficient was 0.06, which is well within the range of effective boundary lubrication. With repeated passes over the same surface the friction coefficient decreased to less than 0.04 where it remained for in excess of one and one half million repeated passes over the same surface. It should be noted from figure V-7 that the film was only 2000 Å thick.

Mechanical parameters such as load and speed can influence friction behavior with lubricant films. The data of figure V-8 indicate that both load and speed exert an influence on the measured friction coefficients for sputtered MoS₂ films. At higher loads the friction was less. Doubling the sliding speed resulted in an increase in friction coefficient.

The real merit in using sputtering as a method for applying lubricant films rests with the superiority of its endurance (wear) life to that of coatings applied by more commonly used techniques. The data of figure V-9 represent the cycles to failure for MoS₂ films applied by three different methods. Burnishing is a process whereby the MoS₂ is mechanically rubbed onto the surface. This frequently used technique gave the shortest life. It was the first of the coatings to fail. A widely used commercial resin bonded film lasted for 100 000 cycles before failing. The sputtered film gave the longest life. This was a 2000 Å thick film. The commercial film by comparison was 130 000 Å in thickness.

A sliding friction experiment with a hemispherically tipped rider sliding on a flat is a extremely severe test of the endurance capabilities of a thin film. The effects of sliding on an MoS₂ film can be seen in figure V-10. At the left is the film appearance prior to sliding. The photograph on the right in figure V-10 is that same surface after sliding. While the film has been severely disrupted by sliding, the underlying nickel is not exposed.

Teflon Films

A material widely used in the field of lubrication because of its inherently good lubrication characteristics is PTFE or Teflon (ref. 5). Teflon has been used primarily for machined parts such as bearing cages in ball bearings. Attempts to use Teflon as a thin film on surfaces in need of lubrication have not been too successful because of the poor bond that develops between Teflon and the substrate surface to be lubricated. In general, the bond has been mechanical in nature and its strength has depended on the surface topography of the substrate. The more effectively the film could be "keyed" into surface irregularities, the better the resulting bond.

Recent studies in our laboratory with the field microscope indicate that chemical bonding of Teflon to substrates can be achieved if a metal surface to be contacted by the Teflon is atomically clean (ref. 6). Such cleaning can be achieved in the sputtering apparatus by the argon bombardment of the surface with the dc bias prior to deposition of the film material. Thus, better bonding of Teflon to surfaces to be lubricated should be achieved by sputter deposition.

Teflon was therefore deposited on various surfaces by sputtering. The resulting films were very dense, uniformly covered the surface, and were very adherent. Figure V-11 is a transmission micrograph of a Teflon film which had been applied to a nickel substrate and the substrate subsequently etched away. The film is free of any pin holes or other obvious defects.

While little concern is necessary for the deposition of elemental metals by sputtering with compounds as was mentioned earlier, concern must be exercised over the possibility of compound decomposition. With polymers even greater concern is warranted. Early experimental attempts at sputtering Teflon at too high power levels resulted in degradation of the polymer on the target surface. The target surface was covered with a carbon film. When, however, the proper power levels are employed, Teflon can very effectively be sputtered.

The data of table V-2 are the results of a quantitative analysis of sputtered Teflon films at various rf power levels. Data for the original or un-

TABLE V-2. - QUANTITATIVE ANALYSIS FOR ORIGINAL
AND SPUTTERED PTFE

Experi- ment	Type of Teflon	Carbon, wt. %	Fluorine, wt. %	rf experimental conditions
1	Original Sputtered	24. 16 33. 89	75. 32 65. 34	Input, 430 W; dc voltage, 600 V; target (ac), 1. 7 kV; argon pressure, 20 μ
2	Sputtered	32. 16	67. 79	Input, 250 W; dc voltage, 400 V; target (ac), 1. 1 kV; argon pressure, 12 μ
3	Sputtered	27. 78	71. 91	Input, 220 W; dc voltage, 325 V; target (ac), 1 kV; argon pressure, 4 μ

sputtered material are also included for reference purposes. Examination of the data indicate that the lower the power level used the more closely the resulting sputtered Teflon film approaches the original unsputtered material in composition. At high power levels, carbon to fluorine bond scission occurs with the result that carbon concentration in the film is greater than in the original material. The fluorine is lost to the vacuum system, presumably in the polymer transport process. Thus, very careful control of power is required when sputter depositing polymers such as Teflon.

A question frequently asked with respect to the sputter deposition of films is what effect does the process have on the temperature of the surface to be coated; that is, is the substrate heated by sputtering? In order to demonstrate that the surface to be coated is practically unaffected by the process, Teflon was sputtered onto a piece of paper. A photograph of the Teflon coated paper is presented in figure V-12. Careful examination of the paper after application of the coating revealed no evidence for any damage to the paper.

CONCLUDING REMARKS

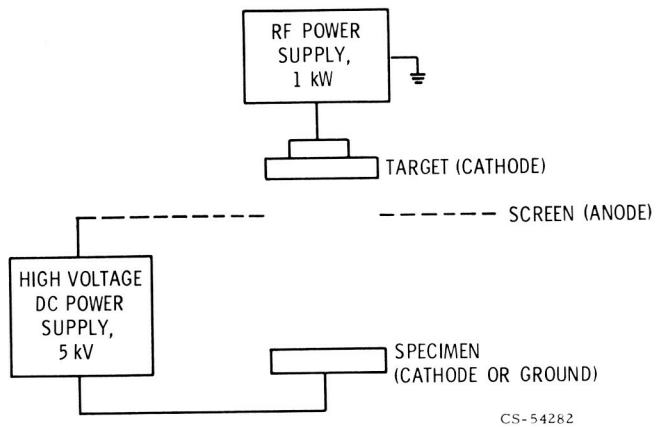
Sputtering has been used very effectively for the deposition of solid film lubricants. Both MoS_2 and Teflon, two widely used solid lubricant materials, have been applied to a variety of substrates by sputtering. The resulting lubricant films are dense, pore free, and adhere to the surface to be lubricated in a manner far superior to that obtained with other available coating techniques. The films provide effective boundary lubrication and exhibit both low friction and wear. The endurance lives obtained with sputtered MoS_2 films only 2000 Å in thickness are markedly greater than those obtained with present commercially available coatings 130 000 Å in thickness.

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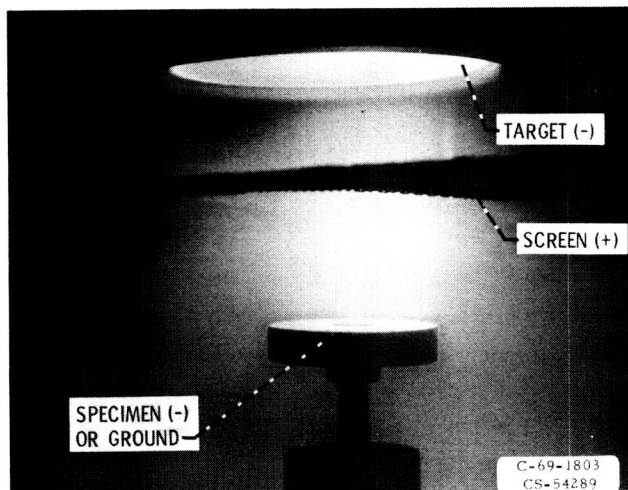
SPUTTERING APPARATUS

RF SPUTTERING SYSTEM WITH DC BIAS



(a)

RF WITH DC BIAS DURING SPUTTERING



(b)

Figure V-1

DARK FIELD TRANSMISSION MICROGRAPH OF MoS_2 FILM



Figure V-2

ELECTRON DIFFRACTION PATTERN OF SPUTTERED MoS_2 FILM



Figure V-3

BALL BEARING ASSEMBLY COMPLETELY COATED WITH MoS_2
FILM BY RF SPUTTERING

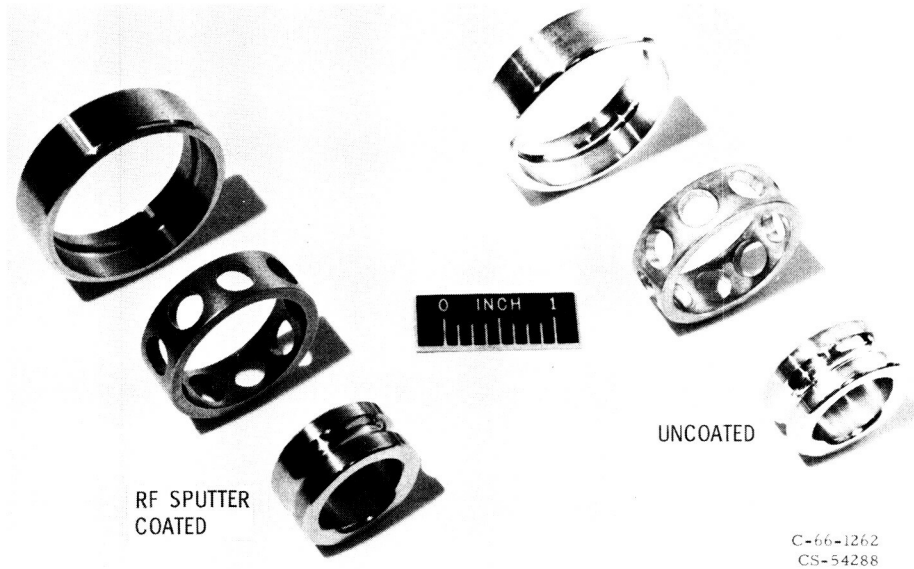


Figure V-4

COMPARISON OF UNCOATED AND RF SPUTTERED
 MoS_2 ON NICKEL AND INCONEL TENSILE
SPECIMENS AFTER FRACTURE

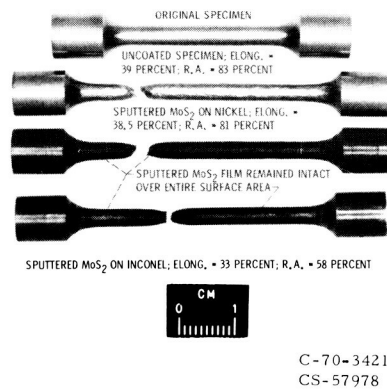


Figure V-5

FRICTION OF NIOBIUM SLIDING ON NIOBIUM WITH AND WITHOUT A SPUTTERED MoS_2 FILM
(PRESSURE, 10^{-11} TORR; LOAD, 250 g; SPEED, 5 FT/MIN)

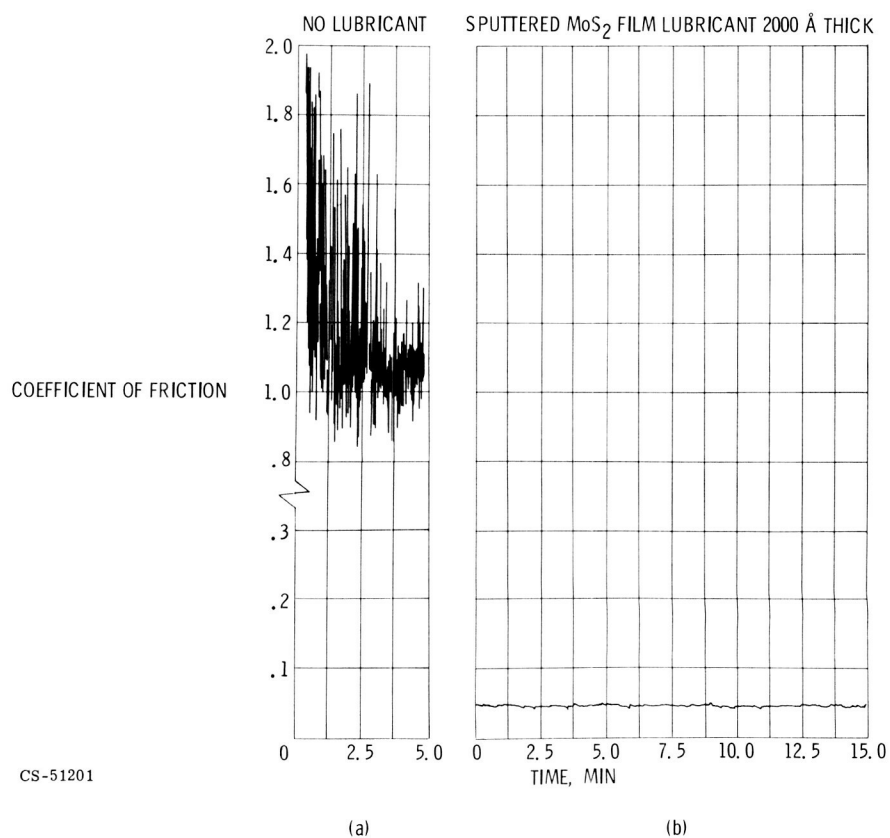


Figure V-6

INITIAL COEFFICIENT OF FRICTION OF 440C STAINLESS STEEL SLIDING ON 440C
STAINLESS STEEL COATED WITH RF SPUTTERED MoS_2 (2000 Å)
(IN VACUUM; LOAD, 250 g; SPEED, 50 RPM)

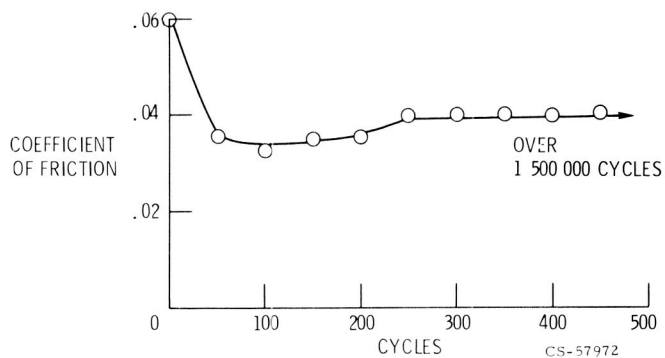
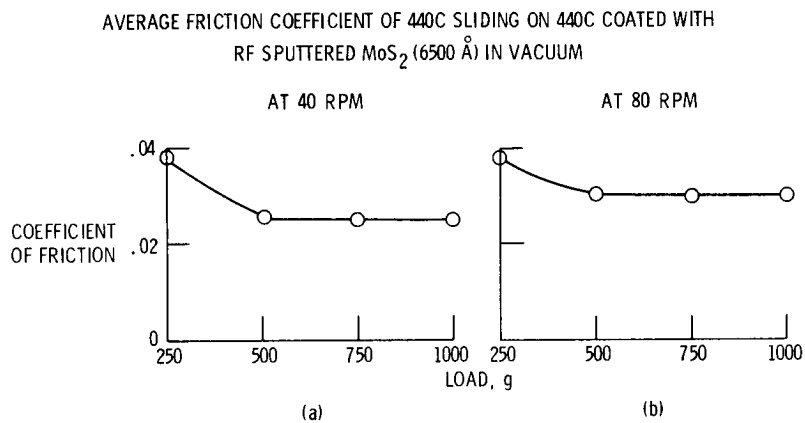
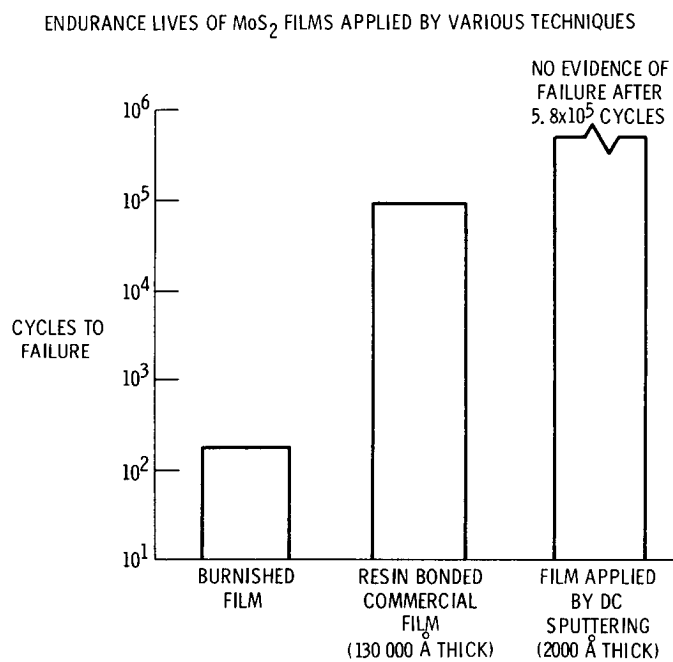


Figure V-7



CS-57973

Figure V-8



CS-51197

Figure V-9

COMPARISON OF SCANNING ELECTRON MICROGRAPHS OF AS-SPUTTERED MoS_2 (2000 Å) ON
NICKEL SURFACE AND FRICTION WEAR TRACK AFTER SLIDING

AS-SPUTTERED MoS_2 FILM WEAR TRACK AFTER SLIDING

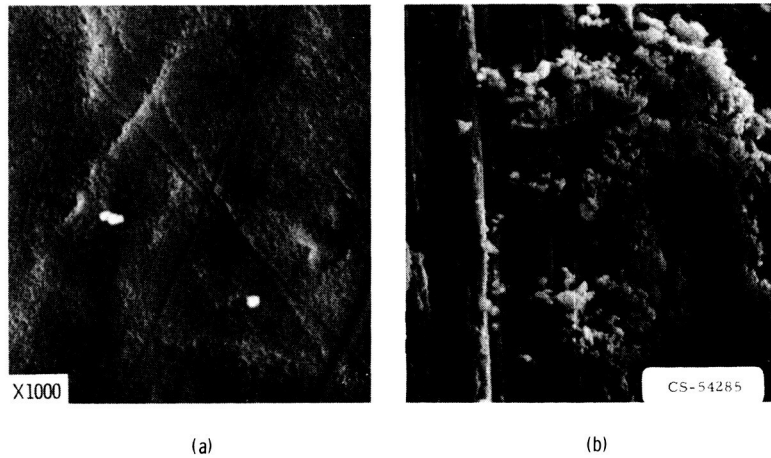


Figure V-10

TRANSMISSION MICROGRAPH OF SPUTTERED TEFLON ON NICKEL

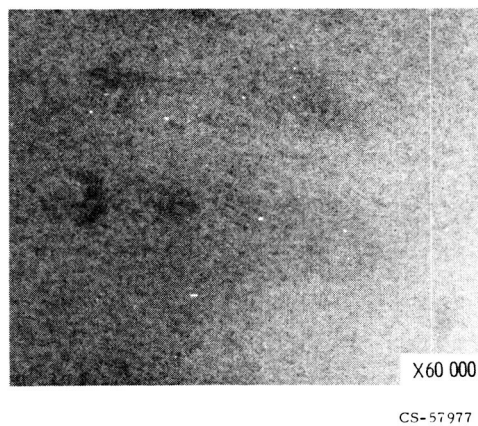
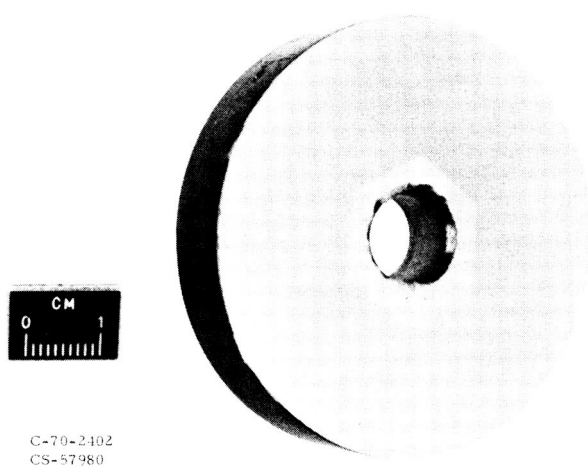


Figure V-11

SPUTTERED TEFLON ON PAPER



C-70-2402
CS-57980

Figure V-12

VI. DEPOSITION OF METAL AND ALLOY COATINGS BY ELECTRON-BEAM ION PLATING

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Until recently, the ion-plating process has been generally limited to the deposition of low-melting materials for coating applications. Only research and development type of applications were previously reported for high-temperature materials; they were deposited generally at low deposition rates. However, several electron-beam melting techniques have been investigated at Battelle's Columbus Laboratories which provide methods for evaporating high-melting-point materials within a glow-discharge atmosphere for high-deposition-rate applications. The magnetically focused hot-filament and the cold hollow-cathode electron sources have been studied to evaluate their operational and evaporation-deposition characteristics for the ion plating process (refs. 1 to 3). These electron-beam techniques and the results of past and current experiments conducted using these techniques are described in this paper.

The ion plating process was first reported in the literature by Mattox in 1963 (ref. 4) and is the subject of a government-assigned patent issued in 1967 (ref. 5). Investigations of the process by Mattox were primarily concerned with gold, aluminum, and chromium coatings applied to both metal and ceramic parts (ref. 6). To obtain coatings on ceramic substrates to which a negative potential cannot be directly applied, a screen wire cage arrangement having a negative voltage is used around the parts to accelerate the ions to the parts to be coated. One of the principal early applications was the coating of a uranium reactor core with aluminum for corrosion protection.

An interesting application of ion plating for coating high-strength steel, titanium, and aluminum alloy fasteners with pure aluminum for corrosion protection in marine environments is described by McCrary, Carpenter, and Klein (ref. 7). This work included demonstration of the deposition of uniform and adherent film on screw threads without any buildup at the thread crown. Spalvins, Przybyszewski, and Buckley have reported some useful descriptions of ion plated coatings on complex shapes and of ion-plated coatings of several alloys deposited using flash evaporation (refs. 8 and 9). Gold coatings, 1300 to 1500 Å thick, were deposited on components of a ball bearing and several other complex shapes. Strong bonding of the coating to the substrates and excellent uniformity were obtained. The alloy coatings, which were ion plated using flash evaporation to vaporize the materials into the glow discharge, were lead-tin and copper-gold compositions. The original compositions of the alloys were closely maintained in the deposit using this technique and very good adherence and uniformity were achieved. In these and other references on the process, it is noted, however, that the range of materials which have been ion plated is rather limited and that relatively little information is reported on the interrelationships of the processing variables involved in the plating process.

ION-PLATING PROCESS

Process Description

Ion plating is a comparatively new physical vapor deposition (vacuum coating) process. In ion plating, the source of the coating material and the substrate to be coated are immersed in an inert gas such as argon. The substrate is biased to a high negative potential to start and sustain a glow discharge, especially in the region between the evaporating source and the substrate. As the source is thermally evaporated (or sublimed) and the evaporated atoms pass through the glow discharge region, part of them are ionized. The positively charged evaporant ions are accelerated toward the substrate by a field corresponding to the substrate potential. They arrive at the substrate normal to it and at a very high energy, which implants the evaporant into the substrate and also sputters the substrate surface. At the

substrate-deposit interface, the implanted evaporants intermix with redeposited sputtered atoms from the substrate, forming a pseudodiffusion bond which can assist in forming a coating highly adherent to the substrate.

The ionized atoms are accelerated to the substrate along the electric field lines, which are produced in the dark space region, and they reach and deposit on the back side of the substrate as well as the front. Also, because the mean free path of the evaporated atom is shorter in the glow discharge environment than the distance between the source and the substrate, atoms of the evaporant on the average make several collisions with gas molecules before they arrive at the substrate surface. Many of these atoms are deflected by the series of collisions to the extent that they can reach all surfaces (including the back side) of the substrate which is not in the line of sight of the evaporating source. Because of these two effects, ion plating has good "throwing power" to coat all surfaces of a part and is not a direct line-of-sight coating process.

Advantage and Disadvantage

Based on the process characteristics as indicated above, ion plating has the following key advantages for various applications:

- (1) It avoids exposure of the part to be coated to reactive gases or liquids. For example, hydrogen embrittlement is not encountered.
- (2) The part to be coated can be maintained near room temperature or can be heated or cooled. Temperature-sensitive materials, such as age-hardened alloys, salts, rubbers, and plastics, can be coated.
- (3) Excellent adherence is usually obtained even between some combinations of materials that normally do not form adherent interfaces. The careful cleaning, pretreatment, and handling steps often required for other coating methods are usually not necessary for ion plating.
- (4) The method has good "throwing power" and quite uniform coatings can be deposited by ion plating without rotating the part. Buildup at corners of parts also is not encountered in this process.

The first two advantages, typical of all three of the vacuum deposition processes (vacuum-evaporation, sputtering, and ion plating), permit the general observation that any material can be coated with "almost" any other material by these processes. The latter two advantages, unique to ion plating,

point the way to important future applications of this technique.

Disadvantages of ion plating are that masking to block coating of certain areas of some parts is difficult in ion plating because of its throwing power and that direct deposit-thickness monitoring during deposition has not been well developed. It is our opinion, however, that the major obstacles to increased applications of the process have been the lack of development of processing parameters and their interrelationships and of practical source-evaporation systems for ion plating a wider variety of materials.

In explanation of the unique advantages of ion plating, it is noted that the excellent adherence obtained with ion plating, even with low substrate temperature, is the result of the high energy of the ions arriving at the surface of the part. Two effects are involved:

(a) Cleaning of the surface by the bombarding argon and coating-material ions before and during deposition.

(b) The high-energy of the impinging coating ions which produced pseudodiffusion and chemical reaction at the interface of even normally nonadherent combinations.

The throwing power of ion plating results because the effective source of the coating ions is the negative glow region of the dc glow (gas) discharge which surrounds the part to be coated. These ions are accelerated to all surfaces of the part (inside the negative glow region) and has across it most of the field gradient (voltage drop) of the discharge.

Process Parameters

The ion-deposition process, regardless of which electron-beam technique is used, requires control of the following process variables to achieve a coating with the desired characteristics:

- (1) Glow-discharge pressure
- (2) Evaporant flux (electron-beam power)
- (3) Substrate voltage and current
- (4) Source-to-substrate distance
- (5) Substrate geometry
- (6) Substrate temperature.

The glow-discharge pressure and the evaporant flux are the foremost parameters to be considered for the ion-plating process. They affect both the

ion-deposition rate and the uniformity of the coating. In this work, the discharge pressure was investigated from 1 to 30 microns under various conditions. The evaporant flux was measured in terms of the electron-beam power applied to the vapor source and was investigated from 1 to 10 kilowatts.

The substrate voltage in a diode configuration as used in this study provides two conditions for the coating process. First, it supplies the electrons to initiate and to sustain the ionization of the vapor atoms and molecules, and second, it accelerates the vapor ions to the substrate. Since all of the elements ionize at less than 25 electron volts, only a low voltage is necessary for ionizing the atoms. However, the potential drop from the ionized plasma to the substrate determines the impact-momentum at which the ions arrive at the substrate surface. This energy-transfer phenomenon determines how many surface atoms will be sputtered away and the adhesion of the resultant coating. The substrate voltages used in the work reported here were from 800 to 2000 volts dc.

The number of ions arriving at the substrate is measured by the ion current flowing to the substrate. The current density on the substrate is also a measure of the heat to be dissipated at each voltage level. The temperature of the substrate, particularly of the surface, is directly influenced by the power density of the arriving ions. The substrate temperature is important in controlling the mechanical properties of the deposit, particularly the ductility. In some coating applications, where high substrate temperatures are required to achieve the desired mechanical properties of the deposit, external heating is required to obtain the proper substrate temperature. The substrate temperature strongly influences the metallurgical structure and the properties of the deposit and must be carefully considered for controlling these characteristics, especially for thick deposits. Ion bombardment is also important in that argon ions clean the substrate surface before and during deposition. The desired power density on the substrate must be determined for the particular materials used. Typical current densities are in the range of 0.4 to 0.6 milliamperes per square centimeter.

The source-to-substrate distance and the substrate geometry are physical variables that affect the deposition rate and characteristics. Special attention must be given to selecting the ion-plating parameters for the particular coating application of interest.

The deposition rate of ion plating depends on all of the six process conditions listed. Varying any one of them will affect the deposition rate and the resulting coating characteristics.

ELECTRON-BEAM TECHNIQUES AND PROCEDURES

There are several electron-beam heating techniques that have been investigated for melting and vaporizing materials within a glow-discharge atmosphere. Described here are two primary types of electron-beam techniques that have been investigated at Battelle's Columbus Laboratories; these are the hot-filament and the hollow-cathode types of electron sources. Some of the heating sources of these types have been used in the vacuum-evaporation process of physical vapor deposition for many years. In that process, high-density electron beams can be obtained for very effectively melting materials; the high-vacuum atmosphere usually used in evaporative coating protects the electron-emitting filament from reactive gas atoms and high densities of bombarding ions.

Hot-Filament Electron-Beam Techniques

In the conventional electron-beam gun the hot-filament supplies electrons by the mechanism of thermionic emission. The electrons emitted are accelerated through a potential of a few kilovolts and focused onto the source material by a magnetic field. In this type of gun the electron emitter must operate in a good vacuum because at higher pressure the emitter is subject to extensive sputtering and arc discharge tends to occur between the high-voltage leads and ground surfaces. For these reasons this type of gun was not previously in use for ion plating. Recently, experimental work was conducted at Battelle's Columbus Laboratories which resulted in the successful development of this type of electron-beam system for ion plating (refs. 1, 2, and 10).

A system using a hot-filament electron-beam gun for ion plating is diagrammed in figure VI-1. It consists of (1) a hot-filament electron-beam source, (2) a conductance baffle, (3) a high-voltage substrate holder, (4) a

vacuum system capable of maintaining argon pressure varying from 1 to 50 millitorr, and (5) two power supplies, one to drive the electron-beam source and one to bias the substrate. A significant item in this arrangement is the conductance baffle in which there is a small orifice. The size of the orifice is typically about 3/16 inch in diameter; it can be reduced or enlarged depending on the beam size used. With the argon gas feeding into the chamber from the top and the diffusion pump evacuating from the bottom, the baffle is capable of maintaining the difference in pressure required for ion plating in the upper region of the chamber and at the same time, maintaining a lower pressure in the bottom region permitting the practical operation of the hot-filament electron-beam gun.

The electron-beam gun used in this developmental work was a rod-fed, 10-kilowatt, single-position, 270° beam source. This gun utilizes X and Y water-cooled deflection coils with flush magnetic poles, a water-cooled copper hearth, the 270° deflected beam for increased filament life, and the rod feeding of the source material. It employs a six-turn, 0.030-inch-diameter, tungsten filament and produces an arrow-head shaped spot 3/16 to 1/4 inch long, depending on the filament to beam former spacing and on the size of the orifice in the conductance baffle where the beam enters the glow-discharge region. For process coating applications, the rod-fed type of mechanism was chosen to feed the source material, which was nominally 1-inch in diameter and 10 inches long in the work reported here. This method provides a large inventory of evaporant for continuous operation and provides precise control of the height of the melting pool. A gun with pocket hearth may also be used to contain the evaporating melt, which can then be replenished by wire or powder-feeding techniques.

The process operational procedures for the hot-filament technique of ion plating are described as follows. The two regions of the vacuum system are evacuated below 1×10^{-6} torr and the discharge region backfilled with argon to a pressure in the range of 5 to 50 millitorr. The electron-filament region of the system is maintained between 10^{-4} and 10^{-3} torr. The substrates are ion cleaned at 2000 to 3000 volts dc for 10 to 15 minutes. The discharge pressure is then adjusted to the desired coating pressure. The electron beam is initiated, and the desired evaporating power level obtained. At this time, the electron-beam power and the discharge pressure are held

constant, and the shutter is opened to commence ion plating; these conditions are then held constant during the period of deposition.

Figure VI-2 shows one of the vacuum systems used in the experimental work and shows the hot-filament type of electron-beam ion-plating process in operation. Note the electron-beam as it emerges from the orifice in the conductance baffle and impinges upon the melting source material.

The system is a double bell-jar type with an oil diffusion pump and a blank-off pressure of below 1×10^{-7} torr. The lower baseplate, the electron-beam gun, and the multiple-hole feedthrough ring with the necessary feedthroughs were assembled together as a unit. The bell jars, conductance baffle, and top plate can be independently removed. The top plate holds the Pirani gauge, the feedthroughs for sustaining and controlling the glow discharge, and the high-voltage substrate holder.

Hollow-Cathode Electron-Beam Techniques

Because there can be various physical configurations of a hollow-cathode electron-beam source, a typical size and shape designed for up to 10 kilowatts of beam power will be used as an example in this paper. Larger and smaller sizes and different designs for various power levels can be used for ion plating.

A diagram of an experimental ion-plating system using a hollow-cathode electron-beam gun is shown in figure VI-3. The construction of a typical 10-kilowatt hollow-cathode electron-beam source consists of a hollow cylinder or sphere that has an aperture typically 0.25 inch in diameter, depending on the diameter and length of the gun. The wall of the gun can be solid, perforated metal sheet, or screen. In operation, the gun is immersed in an argon atmosphere and biased to a negative potential to initiate a glow discharge. As soon as a gaseous discharge is initiated, an electron beam is emitted from the aperture. The electrons are not supplied by a hot filament in this type of gun. Rather, they are generated by (1) the field and thermionic emissions from the inner surface of the cathode which is heated to a very high temperature by ion bombardment, (2) the ionization of the argon gas inside the hollow region of the gun, and (3) the emission of secondary electrons from the inner surface of the cathode wall due to ion bombardment.

In the case in which electrons are generated by the combination of the field and thermionic emissions and the secondary electron emission due to ion bombardment, the discharge is characterized by high current and low voltage. It is referred to as the hollow discharge mode (HCD) and the gun is commonly called the hot hollow-cathode gun. The electron density inside the hollow region is several orders of magnitude higher than that near a plane cathode in a normal glow discharge for the same discharge current density. Because of this particular property, the hollow-cathode electron-beam gun in an HCD has been widely used as electron source for vacuum welding, drilling, and melting (refs. 11 and 12). However, the electrons emitted are not well collimated; an electromagnetic field is necessary to focus the electron beam.

In the case in which electrons are generated by the ionization of the argon gas inside the hollow region of the gun and the emission of secondary electrons due to ion bombardment, the discharge is characterized by low current and high voltage. It is known as the electron-beam mode discharge (EBMD; refs. 13 and 14). Operating in this mode, the gun emits a well collimated electron beam from the aperture. It can switch to the HCD if it is given a suitable condition, such as higher gas pressure or rf power excitation. Because the EBMD gun operates with the cathode at relatively low temperature, it is sometimes called the cold hollow-cathode gun. It also has the capability of emitting an electron beam of very intense power. Applications of this gun in vacuum welding and melting have been reported (refs. 15 and 16).

The hollow-cathode guns of both types have these common advantageous features: (1) they have no hot filament to burn out, (2) they can operate at glow-discharge pressures, and (3) they are easy to design and construct. Their primary disadvantage is that the gun is sputtered in the process and shielding is necessary in many applications to keep sputtered atoms from depositing onto the substrate. In some applications, the gun can be constructed from the same or similar materials as the coating materials so that this sputtering effect does not affect the composition of the deposited coating.

Many types of hollow cathode guns in cylindrical and spherical shapes of different sizes have been investigated. Experiments and results with one typical design cylindrical gun are presented here. The system used is shown schematically in figure VI-3. The gun is 2 inches in diameter and

4 inches long, and the diameter of the aperture is 0.25 inch. The gun face constitutes one of the circular disks of the cylinder; it is made into a concave cone shape for the purpose of facilitating the EBMD. The gun is mounted to a high-voltage post at the other circular disk of the cylinder. The cylinder wall and the cone-shaped gun face are made of molybdenum screen and the back side of the gun is made of stainless steel. The source material is placed in a water-cooled copper crucible. The substrate is biased to a negative potential during the ion-plating process.

The cathode gun is operated in a vacuum chamber in which the pressure is maintained at a fixed value between 1 to 50 millitorr by introducing a controlled inert-gas leak and continuously pumping the gas. The anode is the grounded surface of the chamber.

In the above arrangement, the steady conventional HCD can be easily obtained when the gas pressure is above 20 millitorr. As pressure is reduced, the discharge voltage will remain quite constant until a critical pressure is reached at which the discharge will switch abruptly to a different mode, which is also steady but is operative over a much narrower pressure range. This is the electron-beam mode discharge. A luminous beam is formed originating inside the aperture and extending out in a straight line column. The operating pressure range of the EBMD is limited by the extinction of the discharge and the transition to the conventional HCD for any given size of cathode gun.

The general operational characteristics of the hollow-cathode electron-beam guns are determined as a function of the gas pressure, cathode diameter, cathode mesh or perforation size, and cathode aperture. For a certain cathode diameter the cathode gun will operate steadily, producing a well collimated electron beam with a range of cathode potentials and operating pressures. The performance of the gun will become more and more pressure sensitive if the power is increased (which is done by increasing the pressure closer to the upper limit). The operating pressure of a gun will increase with decreasing gun diameter. For the same diameter the cathode guns having screens of higher transparency will yield higher beam currents than the guns having screens of lower transparency. This result agrees with those reported previously (ref. 17). The voltage-current (V-I) characteristics of the 2-inch-diameter, 4-inch-long, hollow-cathode gun which was used is shown in figure VI-4.

The procedure for using the cold hollow-cathode electron-beam gun for ion plating is initiated by backfilling the vacuum chamber with argon to approximately 30 millitorr from the initial pressure of 1×10^{-6} torr. At 30 millitorr the substrate is sputter-cleaned by applying 2000 volts on the substrate for 10 to 15 minutes. After the substrate has been cleaned, the gun is energized to operate in the HCD. At this stage, the chamber pressure is gradually increased.

If the pressure is reduced to about 3.2 millitorr, the discharge will switch from HCD to EBMD. By carefully adjusting the gas pressure and the potential applied to the gun, the desired electron-beam power is attained, and the source material is evaporated in relation to the applied power. When the shutter is opened, ion plating is started and is continued until the desired coating is achieved.

The techniques and procedures described above for both electron-beam heating techniques are typical of those that we have used for the ion-plating process; they may be modified depending on the specific coating application. The major factors that are considered in choosing the appropriate procedures for a specific coating application are the compatibility of the coating and the substrate materials, coating adhesion, properties of the deposit, and length of time required to complete the coating process.

EFFECTS OF ION-PLATING PROCESS PARAMETERS

Because of the number of process parameters that affect the electron-beam ion-plating process, most of the data presented in this paper are based on the variation of the glow-discharge pressure and evaporant flux. These two parameters are important because the process is quite sensitive to their changes and they strongly influence the resulting deposit characteristics. The other parameters were generally held constant in the experiments reported here.

The coating uniformity was found to be strongly dependent on the discharge pressure. As indicated in table VI-1, the uniformity of coating on a given part increases from 0 to 100 percent as the discharge pressure increases from 5 to 25 microns, with other conditions held constant. The uniformity of a coating on the back as compared with the front of a part

TABLE VI-1. - EFFECT OF DISCHARGE PRESSURE
ON UNIFORMITY OF ION-PLATED COATINGS

[Evaporant flux was constant for all experiments; hot-filament electron gun was used for evaporation.]

Discharge pressure, mm Hg	$\frac{\text{Thickness on back surface}}{\text{Thickness on front surface}} \times 100,$ percent
5×10^{-3}	0
10	50
25	100

decreases as the flux of evaporant (coating) material increases to a high level. This is due to direct line-of-sight deposition of un-ionized coating atoms onto the surface of the part facing the evaporating source material. As the evaporant flux is increased, the discharge pressure and/or other process conditions must be changed to maintain uniformity of the coating on a part.

The effects of the discharge pressure on the rates of deposition and resulting coating uniformity are illustrated in figure VI-5. These curves show the effects for a flat-plate geometry for one set of conditions of (hot-filament) electron-beam power, source-to-substrate distance, and substrate voltage. Since these curves are for specific conditions, they should not be considered process-limiting cases. Rather, they are shown as being typical of the type of interrelationships that we have found for various coating materials and ion-plating conditions.

Other geometries such as cylinders and spheres have curves that are similar but that depend on specific conditions and parameters used. For each coating application, the process characteristics must be determined for the specific size and shape of the substrate. Once these parameters are established, they can be very easily reproduced from part to part.

Because the cold hollow-cathode electron-beam gun is pressure sensitive as indicated earlier, the method of increasing the gas pressure in order to ion plate front and back coatings of the same thickness cannot be used.

Therefore, the method of increasing the source-to-substrate distance is used. The relationship between the ratio of the back-to-front coating thicknesses and the source-to-substrate is shown in figure VI-6. In this series of experiments, the argon gas pressure was 3.2 millitorr, the electron-beam power was 5.1 kilowatts, and the source material was Type 304 stainless steel. It was found that the ratio of 1.0, which is usually desired, was attained when the source-to-substrate distance was 8 inches or more, which is generally a convenient distance in ion plating.

The deposition rate is an important factor in determining both production capabilities of the process and properties of the deposit. The deposition rate depends on many variables such as the electron-beam power, the source-to-substrate distance, the system pressure, and the source material and size. In the evaporation of any specific material by hot-filament electron-beam techniques, the main factor used to control the deposition rate at a fixed source-to-substrate distance and at a specific pressure is the electron-beam power, that is, the beam voltage potential and the emission current. In the case of the electron-beam power supply used in this work, the voltage is fixed at a regulated 10 kilovolts so that the deposition rate is controlled by means of the electron-beam emission current, which is directly proportional to the ac voltage applied to the gun filament transformer. In general, the type of equipment used in this work had sufficient power range to deposit at any desired rate, with the limiting factor being the properties desired of the deposited film. Deposition rates determined for a number of materials are shown in figure VI-7 as a function of the hot-filament electron-beam power for a fixed source-to-substrate distance and source size. Rates for both vacuum evaporation and ion-plating techniques are shown in this figure. It should be noted, however, that data for ion plating were not available for all materials at one discharge pressure and that the curves therefore represent rates for pressures from 10 to 30 microns for the various materials. These curves, therefore, illustrate the range of deposition rates characteristic of this particular type of electron-beam source, but they do not express either upper or lower limits on the rate of deposition. The curve for magnesium shows that a very small change in power is required to obtain a very large change in deposition rate. In contrast to the curve for magnesium is that for tungsten, which shows that a large amount of power is required for a low rate of tungsten deposition.

TABLE VI-2. - DEPOSITION RATES
OBTAINED USING 2-INCH-DIAMETER
COLD HOLLOW-CATHODE GUN

Materials	Source-to-substrate distance, in.		
	4	6	8
	Deposition rate, mil/hr		
Type 304 stainless steel	12	2.6	1.0
FeCrAlY	20	4.4	1.6
Titanium	8.5	2.2	.8

The typical deposition rates for several materials which may be achieved with a hollow-cathode electron-beam source are shown in table VI-2. The gun was operated at 17 kilovolts and at 300 milliamperes and the pressure was held to 3.2 millitorr to produce these rates.

CHARACTERISTICS OF ION-PLATED COATINGS

The coatings obtained by ion plating are characterized in general by good adherence and integrity. Also, there is normally a uniform coating thickness around sharp corners and edges of a part. Figure VI-8 shows a typical structure of strongly adherent FeCrAlY deposited on a copper part. The combination of the high energy of the impinging coating-material ions and the cleaning effect of bombarding ions, as discussed earlier, usually yields strongly adherent coatings that survive typical tape and mechanical tests. Figure VI-9 shows microstructure of a stainless steel coating. Excellent adhesion is obtained with a deposition rate of 20 mils per hour using a discharge pressure of 20 microns and a substrate voltage of 2000 volts. An

adherent coating of zirconium alloy on a steel substrate is shown in Figure VI-10. The density, grain size, and structure of alloys and other coating materials can be widely modified by changing the various coating parameters available in the ion-plating process, including the substrate voltage, substrate temperature, deposition rate, and discharge pressure.

The uniformity of a coating around the corner of a part ion plated with stainless steel (type 304) is shown in figure VI-11. No buildup of the ion-plated coatings is observed at corners or other similar protuberances in the geometry of the parts, in contrast with coatings from most other processes.

The compositions of alloys deposited using the developed electron-beam ion-plating techniques are generally close to those of the source material. Compositions of the source material and the ion-plated deposit for types 304 and 310 stainless steel and FeCrAlY alloy coatings are given in table VI-3. There are differences for some elements that are predictable and the

TABLE VI-3. - CHEMICAL ANALYSIS OF COATINGS

DEPOSITED BY ION PLATING

[X-ray fluorescence analysis in percent by weight.]

Material	Cr	Ni	Fe	Mn	Si	P
Type 304 stainless steel:						
Source material ^a	20	8.5	Bal.	0.75	0.62	0.04
Deposited coating	17.6	7.5	Bal.	.44	.03	.005
Type 310 stainless steel:						
Source material ^a	25.8	19.8	52.6	1.8	----	-----
Deposited coating	25.1	14.6	57	3.2	----	-----

Material	Cr	Al	Y	Fe
FeCrAlY alloy:				
Source material ^a	27.6	6.8	1.95	Bal.
Deposited coating	24.5	4.8	.58	Bal.

^aStandard rod.

same as those usually encountered with electron-beam evaporation techniques. Although other procedures can be used, corrections for such differences can usually be most easily made by modifying the composition of the source material. This was done in the case of the yttrium in the FeCrAlY alloy shown in table VI-3, in which the yttrium content was increased to about 2 percent in the source material in order to obtain 0.5 weight percent in the deposited alloy. When the constituent elements in an alloy source material have widely varying vapor pressures, it is sometimes difficult to achieve the composition desired in the deposit; in these cases, coevaporation techniques are used. The composition of types 304 and 310 stainless steel coating ion plated onto a flat-plate specimen is found to be the same on the front and back sides of the part. Similarly, there was no effect of geometry of the part on the deposited composition of a FeCrAlY alloy.

Using the process parameters and conditions determined as described above, various coating experiments were conducted on a variety of coating applications. Shown in figure VI-12 are parts ion plated for functional applications. The two outside turbine parts are coated with 4-mil-thick coatings of FeCrAlY, and the center blade is coated with 2 mils of gold. The microstructure of an ion-plated FeCrAlY alloy coating was shown in figure VI-10, and the composition of the alloy coating was given in table VI-3. Alloys of FeCrAlY provide superior resistance to oxidation at high temperature for various applications. The gold coating was applied to the vane for experimental purposes. The carbon steel bearing case to the left and the aluminum bearing shaft at the rear are ion coated with 2-mil-thick coatings of 304 and 310 type stainless steel, respectively, for corrosion resistance.

The fasteners and other small parts shown in figure VI-13 were ion plated with aluminum, gold, and stainless steel coatings for corrosion protection and/or hardness requirements. Most of the parts shown are 1- to 2-mil-thick coatings. The pattern shown on the front-center plate was produced by mechanically masking and depositing gold to the desired dimensions. The copper disk in the center was also masked in one area, and beryllium (2 mils thick) was deposited. The Al_2O_3 and BeO insulators to the left were coated with 1-mil thick stainless steel.

Decorative applications of ion plating are illustrated in figure VI-14. Using the developed discharge-cleaning and ion-plating techniques, very adherent and reflective coatings of gold and other coatings were obtained on

a variety of metal tools and parts, plastic objects, and glass bottles and novelties. Some of these objects have also been overcoated with glass by electron-beam ion plating for applications requiring special protection. The two busts shown in the figure were made by a powder-metallurgy (hydrostatic-pressing) process giving a matt finish and then electron-beam ion plated with aluminum (left) and gold (right). The pipe and golf ball are plastic parts and the tools and handle are metal substrates, all of which were coated with gold by ion plating, obtaining extremely adherent coatings.

CONCLUSIONS

Our conclusions based on these investigations of the ion-plating process are as follows:

1. In these studies, relationships between some of the process parameters for ion plating were determined, particularly the effects of discharge pressure versus evaporation and deposition rates.
2. The effects of these process parameters on the uniformity and other characteristics of the deposits were characterized, and the effects of part geometry on the uniformity of the coating and on the composition of alloy coatings were investigated.
3. Using developed parameters, ion plating has throwing power that can achieve 100 percent coating uniformity around parts without rotating them. There also is no buildup at corners of parts.
4. While maintaining most advantages of conventional evaporative coating, such as relative simplicity of production operations, ion plating gives excellent adhesion for new combinations of materials.
5. Versatile electron-beam systems for ion plating have been developed which now permit many more materials to be ion plated and permit high rates of deposition in production operations.
6. Two types of electron-beam guns can be successfully used in ion plating to increase the capability of the process to deposit coatings of high-temperature materials.
7. Coating materials that have been deposited using these electron-beam ion-plating techniques include various pure metals, glass, and complex alloys such as types 304 and 310 stainless steel and FeCrAlY.

ACKNOWLEDGMENTS

The authors wish to thank Mr. C. G. Ruderer, Mr. W. R. Stowell, Mr. G. E. Hoover, and other members of the Battelle Columbus Laboratory staff for their contributions to this work.

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EXPERIMENTAL APPARATUS FOR ION PLATING BY HOT-FILAMENT
ELECTRON BEAM TECHNIQUE

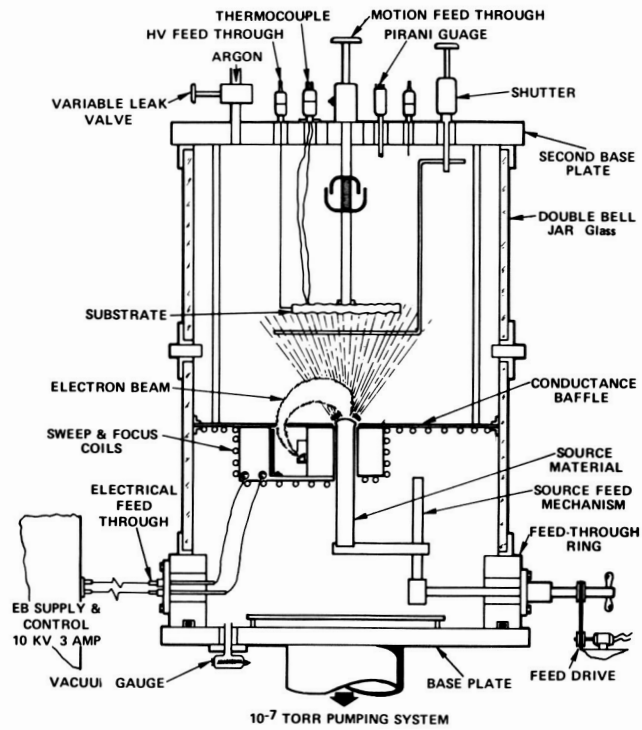


Figure VI-1

VACUUM SYSTEM USED FOR DEVELOPMENTAL WORK
ON HOT-FILAMENT TYPE OF ELECTRON-BEAM
ION PLATING

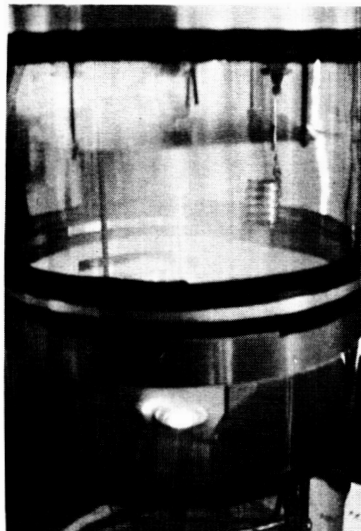


Figure VI-2

EXPERIMENTAL APPARATUS FOR ION PLATING BY HOLLOW-CATHODE ELECTRON BEAM TECHNIQUE

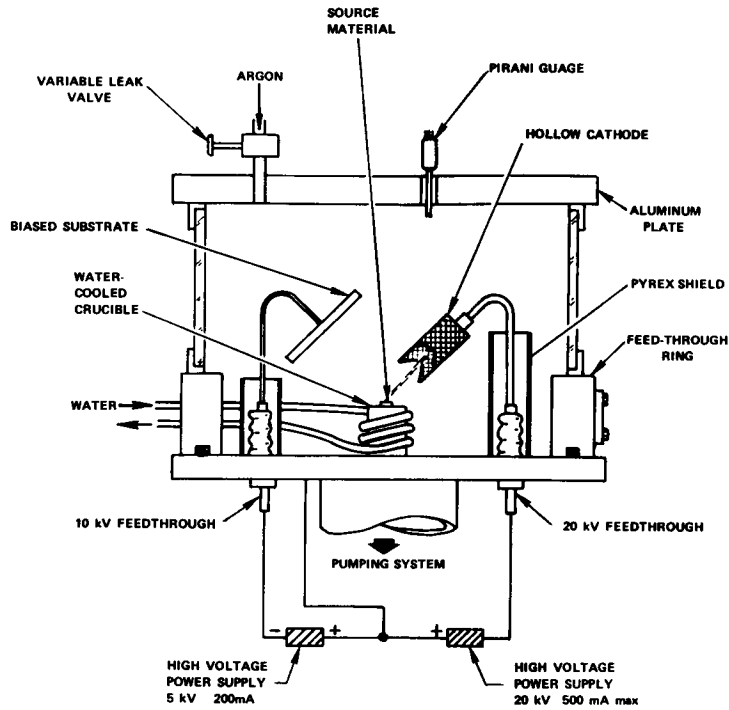


Figure VI-3

VOLTAGE-CURRENT (V-I) CHARACTERISTICS OF HOLLOW-CATHODE ELECTRON BEAM GUN

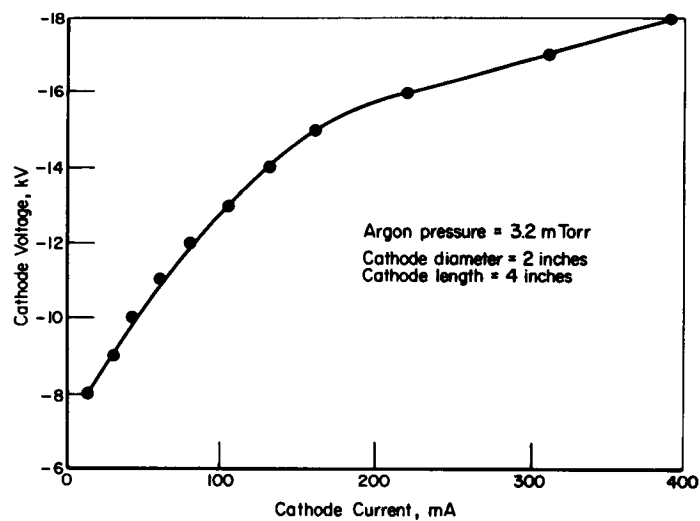


Figure VI-4

RELATIONSHIPS OF ION PLATING PROCESS CONDITIONS FOR A FLAT-PLATE GEOMETRY

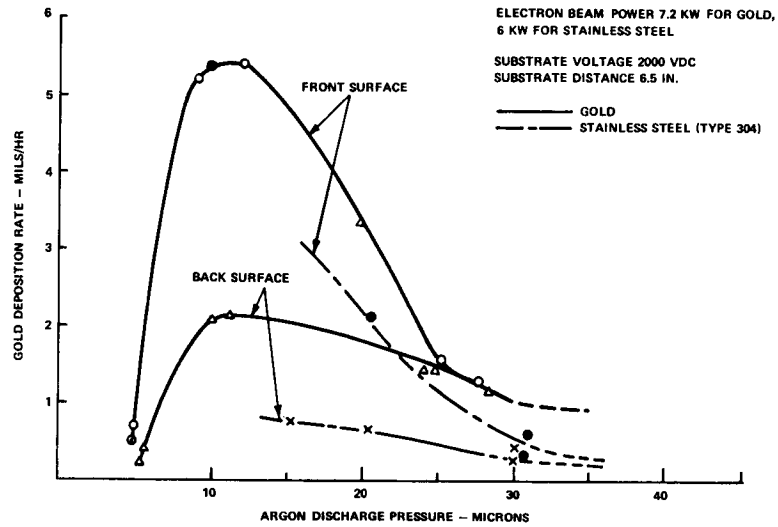


Figure VI-5

EFFECT OF SOURCE-TO-SUBSTRATE DISTANCE ON COATING THICKNESSES ON BACK AND FRONT SURFACES OF A FLAT PLATE

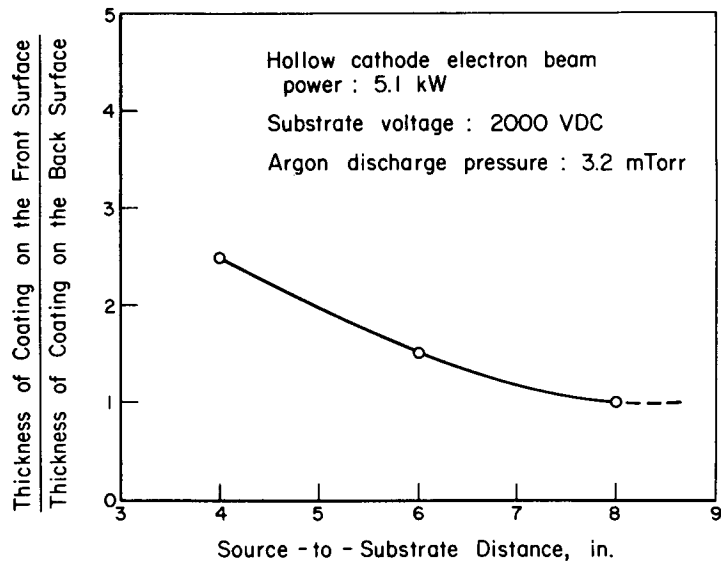


Figure VI-6

DEPOSITION RATES FOR VARIOUS MATERIALS USING ELECTRON-BEAM EVAPORATION AND ION PLATING

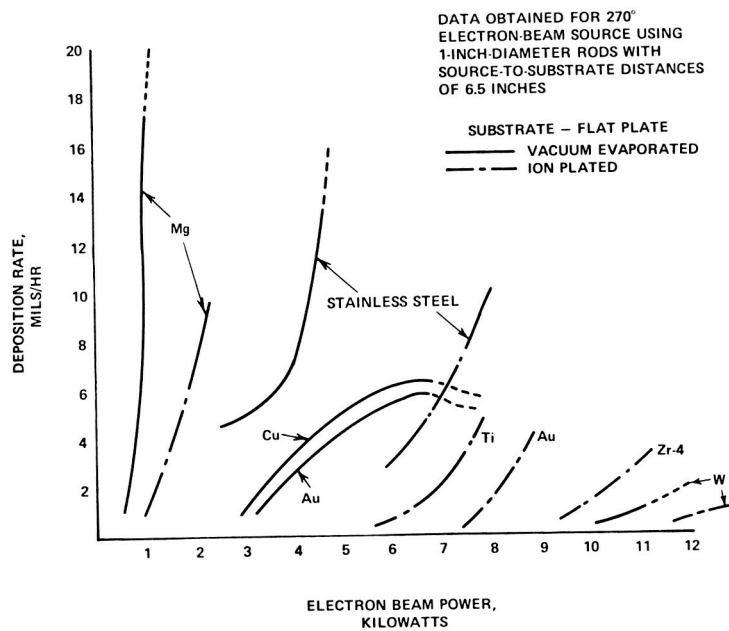


Figure VI-7

TYPICAL STRUCTURE OF ION-PLATED FeCrAlY COATING ON COPPER PART

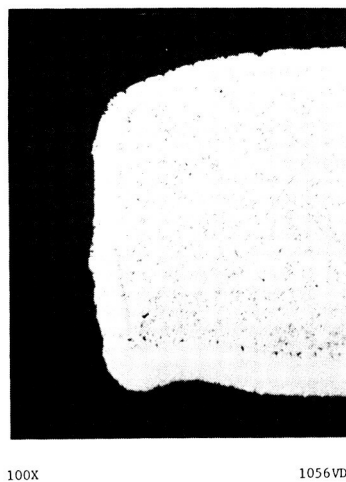


Figure VI-8

COATING OF TYPE 304 STAINLESS STEEL
WHICH WAS ELECTRON-BEAM ION
PLATED ONTO THE SIDE OF A PART

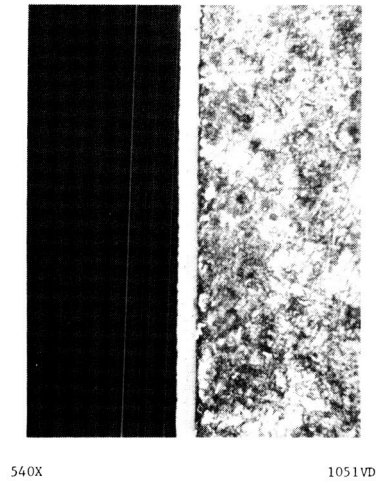


Figure VI-9

ZIRCONIUM ALLOY COATING DEPOSITED
ON MILD STEEL PART BY ELECTRON-
BEAM ION PLATING

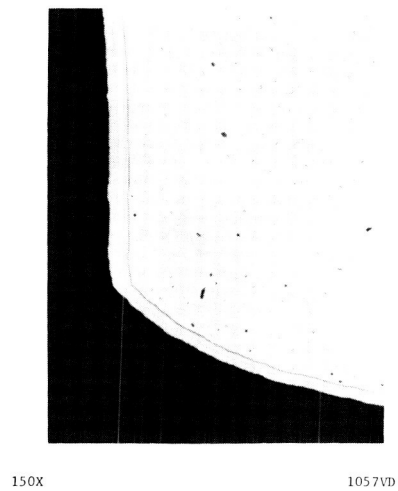
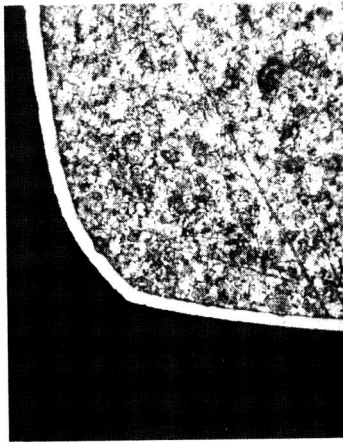


Figure VI-10

COATING UNIFORMITY AROUND CORNER
OF PART IS SHOWN IN THIS PHOTO-
MICROGRAPH OF A PART ION
PLATED WITH TYPE 304
STAINLESS STEEL



213X

1049VD

Figure VI-11

PARTS WHICH WERE ELECTRON-BEAM ION PLATED FOR FUNCTIONAL APPLICATIONS

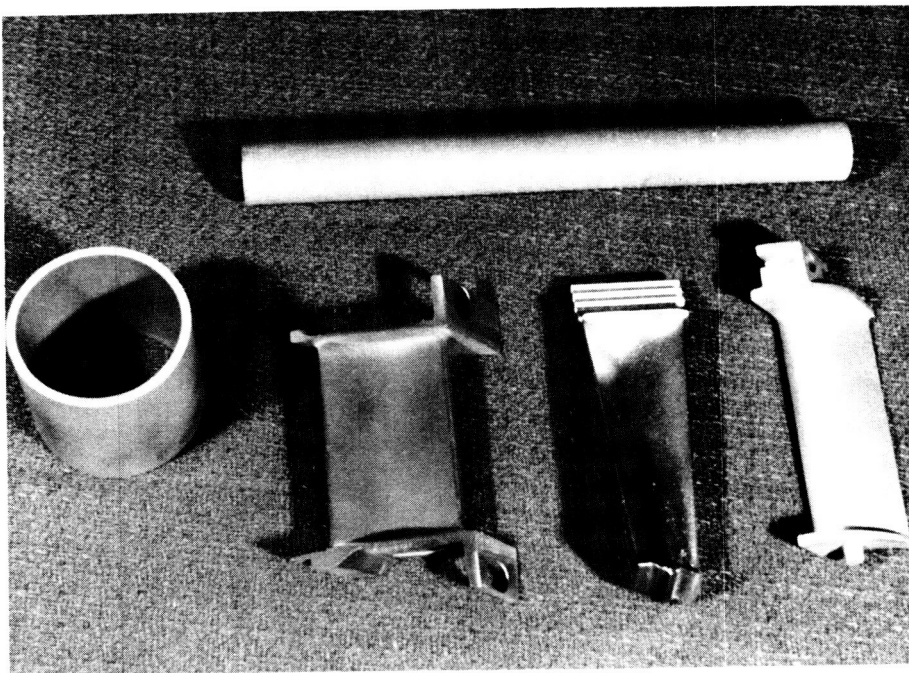


Figure VI-12

FASTENERS AND OTHER SMALL PARTS WHICH WERE ION PLATED WITH ALUMINUM, GOLD, STAINLESS STEEL
AND BERYLLIUM COATINGS

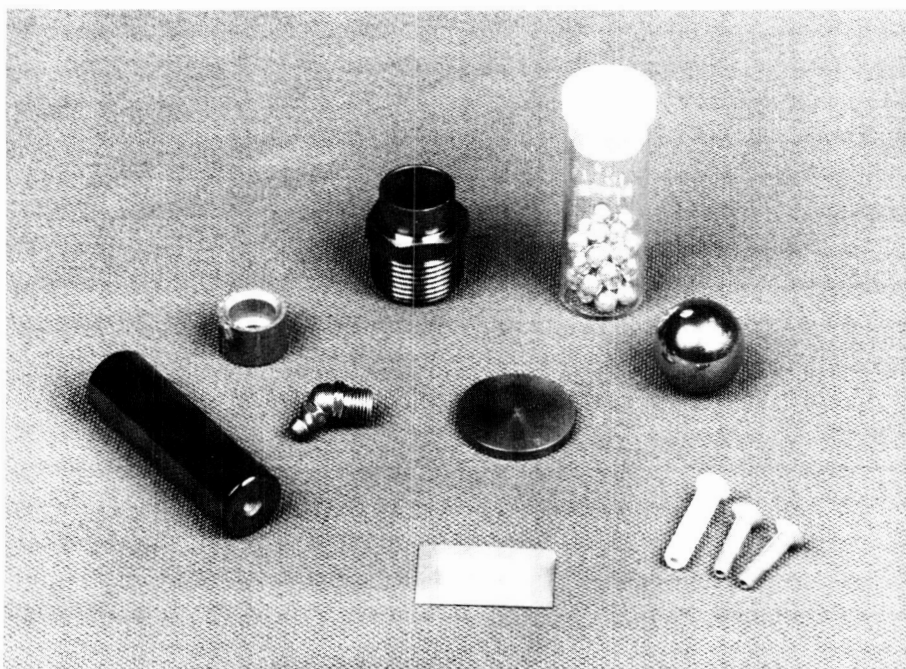


Figure VI-13

DECORATIVE APPLICATIONS OF ION PLATING DEMONSTRATED GOOD ADHERENCE AND HIGH REFLECTIVITY

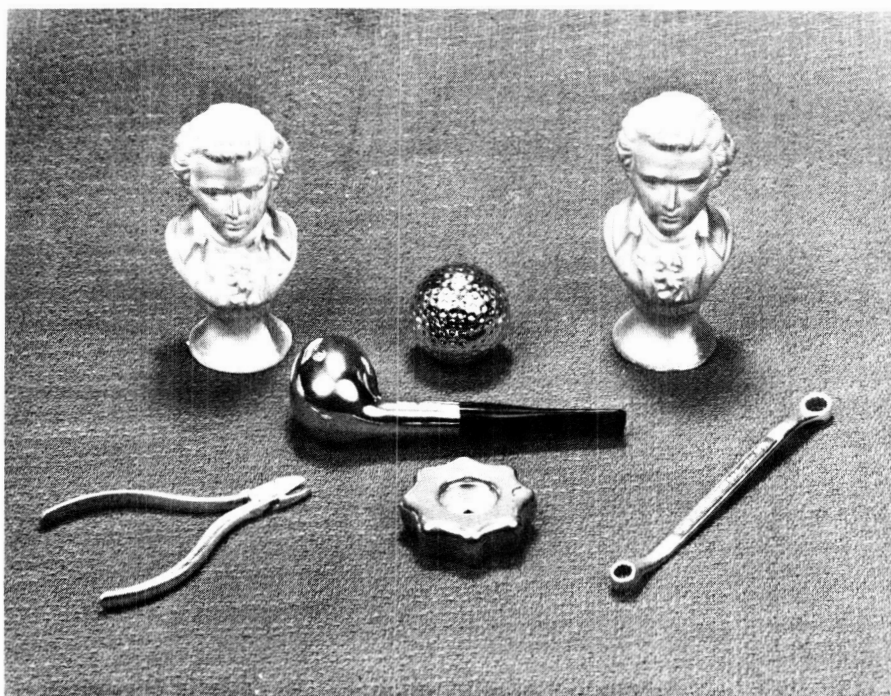


Figure VI-14

VII. INDUSTRIAL POTENTIAL OF ION PLATING AND SPUTTERING

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The coating, cladding, and plating of substrate surfaces is a large and varied industry. As new materials are advanced, engineers, metallurgists and scientists immediately look for methods to coat the surfaces with other materials to achieve still further beneficial properties. As new coating techniques are developed, their use extends and broadens the overall properties of the coated substrate.

In order to select a proper coating material and method for a given substrate material and to effect a desired result, it is necessary to have a broad knowledge of the deposition method as well as knowledge of the properties of materials. The deposition method can be and usually is a major factor in determining the final properties of a coated surface.

It is well known that coatings of various materials can be deposited on surfaces by many methods such as spraying, impingement, vaporization, electroplating, cladding, dipping, etc. All of these have many variations of processing parameters that effect the properties of the finished product. This is also true of ion plating and sputtering.

Nearly all coating processes have a common requirement; that is, the surfaces must be clean to some degree prior to coating, and the substrate surfaces must have some compatibility with the coating material at the energy levels of deposition.

Ion plating and sputtering are similar yet they represent two distinctly different processes. The two processes have a cleaning cycle common to each other. The cleaning aspects of the two processes cannot be over-emphasized, because with ion bombardment surfaces can be cleaned on an

atomic scale, and kept clean during the coating cycle. Most other coating processes have a transfer from cleaning media to the coating media, which introduces possibilities of contamination, especially where oxides are objectionable. Not only does ion bombardment allow extremely clean surfaces; it offers versatility, in that by control of gas mixtures and power inputs, various oxides can be produced under controlled conditions. In some cases, a proper oxide interface promotes adhesion between substrate and coating material. Surface modification can also be achieved by control of ion bombardment cleaning. It is normal practice to use the same type of gas for cleaning as is used for coating. In the ion-plating process the ideal situation is to sputter or ion clean at a fairly fast rate then to sputter at a slower rate during ion plating. This can be achieved by using a heavier gas such as krypton for cleaning, then switching to argon or helium during the ion plating cycle. Generally, however, the higher cost of krypton gas does not warrant its use.

Another important consideration for the user of these two processes is the fact that they are clean and present no particular problem from an ecological standpoint. The only effluent being the inert gas and oil vapors from the vacuum system, which can be easily condensed.

Sputtering for the most part is a coating process by impingement. The good adhesion properties offered is due to the excellent cleaning and high kinetic energies imparted to the coating particles. The sputtering process is theoretically a line of sight process while ion plating follows electrical lines of force. It should be pointed out that by proper positioning of parts, sputtered films will, by gas diffusion, coat around corners. However, in achieving this phenomenon, the depositing particles will strike the substrate surface with less energy than if actual line of sight impingement occurs. This can and does effect the physical properties of the film. Tests of sputtered molybdenum disulfide films on a Hohman A-6 dual rub block tester, shown in figures VII-1 and VII-2, give endurance lives of 5200 cycles for films sputtered at low power levels, as compared with 60 000 cycles for films deposited at higher power levels. Film thicknesses for determining these endurance spreads were controlled at 4000 Å and run at a load of 15 000 psi at a speed of 30 feet per minute.

Several sputtering techniques are available to the user, such as:

- (1) Radio frequency sputtering (offering the ability to sputter non-conductors)
- (2) Diode sputtering with direct current
- (3) Triode sputtering with direct current
- (4) Sputtering with substrate biased
- (5) Sputtering with magnetic fields included in the geometry.

In addition to the power and geometry variations, the user has a choice of gases or mixture of gases to further extend the versatility for coatings with differing physical properties. Examples would be oxides with oxygen mixtures, nitrides with nitrogen mixtures, and carbides with acetylene. Also codeposition of several different materials can be used to form composites. From the general description given, the many possibilities can be seen, and below is a broad list of various advantageous areas of use.

In optics, interference metallic films can be made on glass and glass like materials having electrical conductance with controlled resistance. Reflecting films are also made with good adherence and from a wide choice of materials.

Electrical applications include insulating materials on conductors and, conversely, conductors on insulators. Advantages are the wide choice of materials and close control of electrical resistances. Sputtering is also an accepted process for electronic components, printed circuits, and microcircuits. Magnetic materials may also be deposited on nonconductors.

In the area of tribology lubricating materials such as molybdenum disulfide, calcium flouride, and flourocarbons as well as combinations of materials can be deposited on friction surfaces in extremely thin films thus not affecting close tolerances. These films are especially well suited for precision instrument bearings and moving parts.

Sputtered films of oxides, carbides, and nitrides on cutting tools offer a broad field for investigation. Sputtered films may also be used in chemistry as catalytic films.

Deposition rates for most sputtering applications is slow in comparison to other methods, and it is not implied that sputtering will replace conventional coating methods. It should be pointed out that vacuum techniques have advanced to the point that the process can be automated if volume

warrants, and under these conditions the process is economical in view of its many advantages. The razor blade industry has adopted the process with a great deal of publicity while the electronic industry uses the process for volume production without much fan fare.

The ion plating process is unlike the sputtering process from the standpoint that the coating particles are ionized and follow electrical lines and therefore will coat irregular shaped parts with a good degree of uniformity. In the plating industry the ability to plate recesses and irregular shaped parts is referred to as "throwing power." The ion plating process is excellent in this regard, and, because of its good throwing power masking selected areas require techniques different than normally used in electroplating. Masks generally consist of metal fix-tured to the part.

Ion plating of nonconductors is achieved by placing a conducting grid near the surface of the nonconductor. As the ionized metal coats the grid it is being sputtered off, and thus deposits a conducting film on the nonconductor at which time the ionized metal is attracted to both the grid and nonconductor.

Being a high-energy process, ion plating fulfils the compatibility requirement between substrate and coating material mentioned earlier, and offers some interface alloying between materials not normally compatible. The potentials of ion plating are limited only by imagination and the ability to adapt economical procedures.

It has been the desire of platers to honestly say they could successfully coat various substrates with other materials for many functional reasons. The ion process is a method for insuring a clean, oxide-free surface for bonding and a high energy process for insuring a metallurgical bond.

An excellent example of this was the need for a well bonded coating of 0.020 inch of copper on titanium. Although this can be done with conventional methods, the adhesion is marginal and does not withstand subsequent machining and end use requirements. Our approach was to ion plate copper to a thickness of approximately 0.001 inch and follow this with heavy copper electroplate from a standard sulfate bath. This has worked exceptionally well and gives excellent adhesion as depicted in the photomicrograph of figure VII-3.

The example serves two purposes. First, it shows a clean interface on a material which is extremely difficult to clean of its oxides, and, second, it demonstrates that conventional electroplating can be performed over the ion-plated surface. In addition to this example we have successfully deposited a number of different metals on aluminum, molybdenum, tungsten, beryllium, and magnesium.

Another example of the combination process of ion plating and standard electroplating was the requirement to provide a bright decorative nickel chromium finish on a zinc die cast alloy which would withstand prolonged use at 750° F without blistering or peeling. All attempts with conventional electroplating failed, but by ion plating a substantial copper film followed with conventional nickel chromium plating, the required results were achieved.

We have obtained excellent sliding wear results by ion plating gold on tungsten carbide for seal surfaces working in vacuum. Ion-plated gold has also worked well on cold welding dies, functioning in vacuum, as a non-sticking interface.

Hydrogen embrittlement of highly stressed machine components, characteristic of conventional plating baths, can be eliminated by using the ion-plating process. The advantages over vacuum evaporation is the excellent adhesion of the ion processed coating and improved corrosion. Coating ferrous alloys with aluminum can be easily achieved whereas conventional methods are rather complicated and results are marginal.

The nature of the ion plating process is such that the films are essentially free of porosity and in many cases thinner films should provide adequate corrosion protection. Ion plating of small intricate instrument components will provide adequate corrosion protection as well as lubrication. Tightly adherent coatings on titanium should allow use of the metal in the hot sections of aircraft engines thus effecting weight savings of considerable proportions.

In summary, the sputtering process offers a broad selection of materials for thin films but gives relatively slow deposition rates. The ion plating process offers the possibility of plating most metallic substrates with a wide choice of materials. It has good "throwing power"

and deposition rates are reasonably fast.

Both processes are clean and almost completely free of the ecology problems generated by normal plating operations.

The cost of equipment is relatively high and the learning curve is relatively slow. These two factors, along with a lack of wide knowledge of the processes' possibilities have been deterrents to broad acceptance.

With contract processing facilities available, these deterrents can be overcome, and I feel the processes will be adopted where the final results warrant their use.

DISCUSSION

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Electroplating and sputtering are not really competing metal finishing processes. Electroplating conventionally fills the need for a surface coating on metals and, more recently, on plastics where coating thicknesses between 0.0001 and 0.001 inch are required. Electrodeposited films in thicknesses greater than 10 mils are used to repair or salvage worn parts, to build up functional areas of parts in special sections, or to form free-standing functional shapes, for example, electroformed dies and molds. Electrodeposited films below 0.0001 inch in thickness are frequently denoted as strike or flash coatings and are often used as undercoats to enhance bonding for heavier finishes. Precious-metal coatings have been routinely electrodeposited in film thicknesses between 30 and 100 micro-inches but precise control of film or properties in this category or below is often difficult.

It is below these levels of thickness that sputtering comes to the fore. Sputtering, ion plating, and related procedures can deposit materials as coatings including nonmetallics, pure metals, and alloys in film thicknesses from several hundred angstroms to, in some cases, as high as 50 000 Å (0.0002 in.). In the thicker applications it must be remembered that, from

a competitive standpoint, for thicknesses from 0.0001 to 0.001 inch electroplating of conventional metals had the advantage of being able to plate faster and to cover larger surface areas as well as more highly configured surfaces. Typical deposition rates for sputtering are in the range of 100 to 2000 Å per minute. The overall sputtering operation is somewhat slower simply because it is a batch process and because a vacuum, in most cases, has to be drawn in a chamber before an inert gas - a necessary ingredient for establishing a plasma - can be added. Costwise, \$3000 to \$5000 will allow an operator to establish a modest chromium plating line (tanks, rectifiers, racks, anodes, meters, etc.), while a modest to moderate functional operation in sputtering (vacuum system, bell jar or chamber, power supply, control equipment, and accessories, etc.) may cost between \$8000 to \$38 000 (with automated units and high capacity systems proportionally higher).

In the electronics industry sputtered coatings find applications for protecting metals against erosion, oxidation, and corrosion or for making solderable coatings on glass and ceramics components. Sputtered coatings of gold, platinum, and other precious metals or contact metals are finding use in such components as conductors, the land areas of integrated circuits, resistors, and a variety of piezo-junction devices. As presented earlier, alloys and various ceramics can be sputtered for decorative purposes. These find their ways into glass applications for trophies, bottles, specialty glass caps, and even some fibers and textiles. Because the substrates can be cooled during the sputtering process, films can be applied quite readily to materials such as paper, plastics, fabrics, and other fibrous forms. When compared with vacuum evaporation of metals and alloys (which is primarily condensation oriented and a line of sight operation), sputtering and ion plating can be used more readily to form coatings of difficult to deposit and highly complex alloys, inorganic materials, and high-temperature pure metals, which are nearly impossible to vaporize. Stoichiometry control (or obtaining the same chemical composition of the deposited coating as you started within the target) has been a problem in sputtering some complex compounds and alloys, but a variety of procedures including reactive sputtering and bias sputtering have been effective in alleviating these problems.

In addition to the valuable use of sputtering for solid-film lubricants mentioned in other papers presented at this conference, Professor Wehner has mentioned that a large percentage of the bombarding ion energy appears as heat in the target, necessitating provisions for cooling the target. However, plastics and lower melting or temperature sensitive inorganics and metallic materials can now be coated by sputtering when proper cooling provisions are employed.

In the sputtering processes, dc sputtering was the first process exploited but was only useful in depositing metal films. In the last decade, however, through the advanced developments of such men as Professor Wehner, rf sputtering, which has been discussed at this conference, has been successfully developed and expanded such that a variety of nonmetallic materials and alloys can be successfully used. Another technique, ion plating, discussed here by one of its developers, D. M. Mattox, illustrates that there are a number of variations of sputtering-related processes that have a place in modern coating technology. Radiofrequency sputter etching, reactive sputtering, plasmatonic sputtering, radial sputtering, and a number of other variations provide a fair choice of procedures when one desires to deposit controlled-property ultrathin films with high reliability. The electroplater who produces thousands of parts per hour or per day either in barrel or in rack applications using zinc, copper, nickel, or chromium need not fear that his methods will become obsolete or unused because of this technology. Larger parts and even small parts that must be mass produced with thick metallic coatings will continue to make electroplating profitable. A number of applications are fast emerging in the electronics and aerospace fields wherein thin or ultrathin films of precious metals, inorganics, or ceramic materials and alloys that cannot conventionally be deposited by electroplating are required. These applications will make sputtering attractive and worthy of consideration for the metal finisher who, in the not too distant future, may not simply be categorized as solely an electroplater but as a metal finisher with the knowledge and equipment to coat a variety of components with a variety of materials by a variety of processes.

HOHMAN A-6 FRICTION AND WEAR TESTER

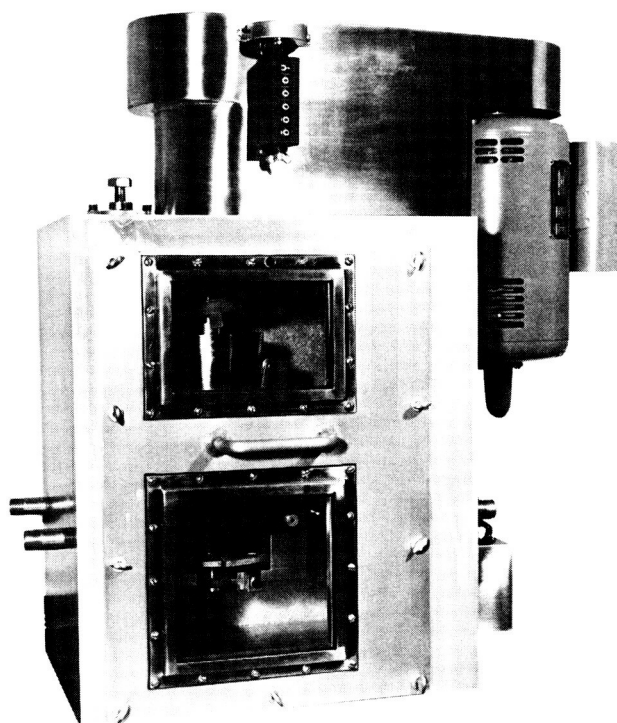


Figure VII-1

CS-62313

ESSENTIAL MECHANICS OF HOHMAN A-6 FRICTION AND WEAR TESTER

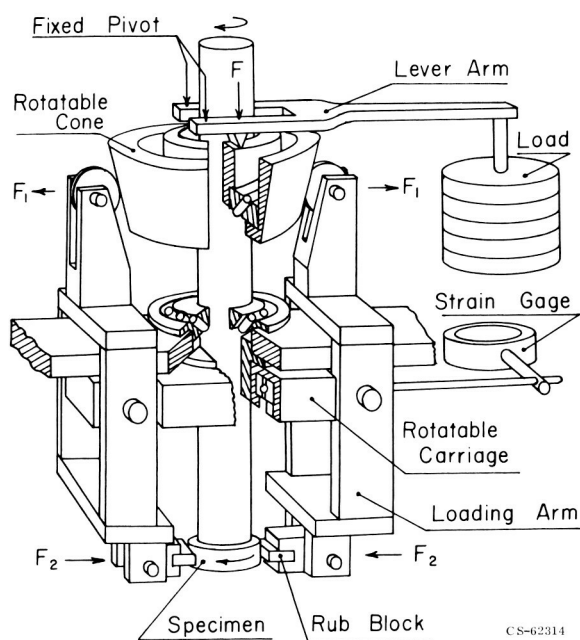


Figure VII-2

CS-62314

PHOTOMICROGRAPH SHOWING EXCELLENT ADHESION OF ELECTROPLATED COPPER
OVER ION PLATED COPPER ON A TITANIUM SUBSTRATE

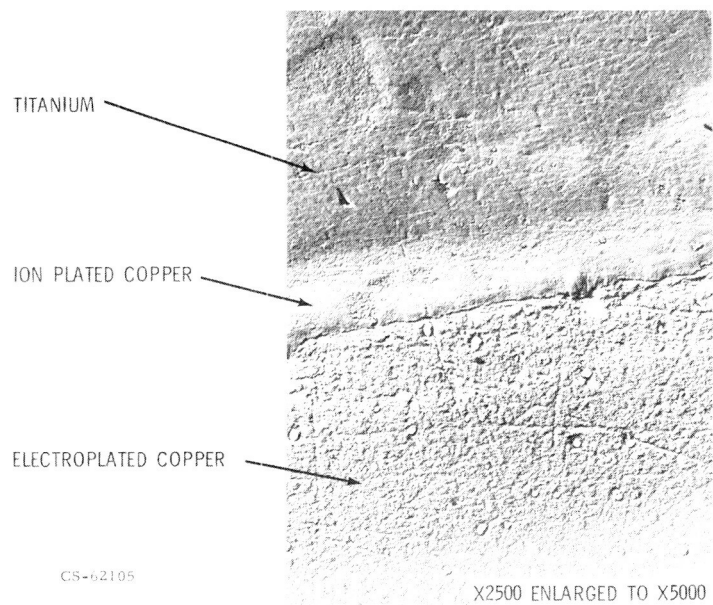


Figure VII-3

VIII. INDUSTRIAL SPUTTERING FOR BETTER DECORATIVE COATINGS

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Louisville, Kentucky 40202

Our purpose is not so much to elaborate on what has been done, but rather to advise you as best we can what needs to be done. We will confine our remarks to one small segment in the decorative field. Our part in that segment is to supply decorative glass and plastic parts for the packaging industry. Specifically, our function has been to achieve adornment of these parts by means of applying metals to a surface of a variety of molded components. This is a still small but growing field. While the use of metals for eye appeal is not new, it has really come into prominence only during the past 20 years. Until our venture into the use of sputtering as a decorative tool, such effects were achieved either by evaporation or silver reduction.

Figure VIII-1 shows a variety of packages which have used one or the other of these processes and are typical of the use of metals for sales appeal. Most of the packages shown have been purchased by companies who rely as much or more on the package to sell their product as on their advertising.

In the early days, little attention was paid to the compatibility of the decorative coating with the product being sold. However, the processes were used usually on only those items whose required shelf life was known to be fairly short; that is, if the coating was good enough to maintain its original appearance for perhaps 4 to 6 months, the coating was considered adequate. This philosophy was largely one generated by necessity, for at that point in the history of the industry, most decorating firms lacked the technology to provide something better. It also was necessary to go to

considerable length to prevent deterioration of the coating by abrasion during shipment. Nevertheless, it was demonstrated time after time that this type of merchandising had a dramatic ability to increase sales; thus, in spite of the shortcomings, the concept grew. As an example, one distiller has records to show that in 1959 a switch from a plain metal stamped closure to a gold metallized jigger cap on his package increased his sales by more than 700 percent in a 3-month period in Washington, D. C. Such trends were obviously picked up by designers throughout those industries whose targets were retail sales. In turn, these companies began to demand better and better quality of the decorative coatings, for, as a result of the shortcomings, complaints from customers came in at an alarming rate. It was not uncommon for a housewife to buy a fancy package of bubble bath only to find that during the first or second use of the product the bottle was left with streaks where the metallic decoration had been entirely removed by contact with the product.

The decorating industry had only one place to turn for help. They, of course, were powerless to change the nature of aluminum or silver, and they could only hope to use those methods available to them for applying such metals and then protecting them the best they could by using improved organic coatings which were rapidly being developed primarily by the paint industry. As improvements were made, it was only natural that buyers of such decorative finishes tightened their specifications so as to be sure of availing themselves of the latest improvements. The progress was rapid; by the middle 60's, it was possible to buy plated glass or plastic parts finished in metallic colors which usually could be expected to withstand the 24-hour immersion test in most alcohol based products and cosmetics. Also, if these parts were carefully prepared for shipment and moved off the retailers' shelves after a reasonable length of time, they would usually last for the useful life of the package. It was not a complete answer, but the improvement was good enough that the design concept was enlarged, and the industry grew. Pressure from the more sophisticated packagers, however, did not alleviate, and more and more demands for tighter and tighter specifications regarding shelf-life and abrasion resistance were made.

Our own company progressed in technology at least as fast as the rest

of the industry, but it was apparent to us that some method had to be found that would allow us both to improve on industry specifications and at the same time achieve our goal without using organic coatings. This philosophy turned us toward sputtering. After considerable testing of laboratory produced sputtered parts, we contracted for a sputtering machine large enough to permit a meaningful capacity for our industry and mechanically versatile enough to handle a large variety of shapes and sizes.

Figures VIII-2 to VIII-7 present the results of this contract. Figure VIII-2 shows an overall view of the machine itself - said to be the largest of its kind in the world. A view of the chamber interior showing the arrangement of the target is presented in figure VIII-3. Figure VIII-4 shows a full load of parts preparatory to entering the chamber, while figure VIII-5 shows the parts loaded ready for closing the door and firing. A full load of finished parts is shown in figure VIII-6. Finally, the finished load is wheeled in for unloading and inspection; then, the fixture is reloaded (fig. VIII-7). The machine was purchased in 1969. After about 1 year of trial runs, it was placed in production of substantial quantities of stainless steel and aluminum coated bottles with a high degree of success. These bottles have been shipped to our customers without the customary tissue wrapping. The standard 24-hour test was rendered meaningless for such bottles, for these bottles have withstood 6 months under the same test conditions without any deterioration.

New tests involving oxidation and high humidity standards have been evolved and accepted by our company. We are quite convinced that in the end sputtering will displace all the other conventional methods of deposition where a high level of quality is of importance. Costs are comparable to conventional methods of deposition where a high quality is important, and because of decreased handling, production losses are substantially less. Our system needs no costly organic base coat application, and top coats are used only in those cases where final color cannot be achieved from the basic alloy for the design in question or when the basic metal is subject to attack by oxidation.

There are, however, obvious improvements which must be made if sputtering is to take the place it rightly deserves in the industry. First of all, at this point, our equipment is limited insofar as decorating plastic

parts are concerned. We are called on to apply metal coatings to closures made from phenolic, polystyrene, and polypropylene materials. Since the heat generated during the sputtering process is higher than conventional methods, outgassing and distortion of these materials are problems. We have worked at some lengths with the resin compounders, and considerable progress has been made toward developing special phenolic resins. It would appear that we will soon be producing phenolic closures on a commercial basis. The sputtered film on all of these materials has every characteristic required except brilliance. The outgassing, of course, is the chief reason for lack of brilliance. It would appear that if the resins could be formulated in such a way as to remove the more volatile material the outgassing would likely be decreased to the point that sputtering could be mostly successfully used. A more fundamental approach undoubtedly will be necessary if we are to achieve satisfactory results when using polystyrene or polypropylene. It is likely that a method of redirecting or dissipating the unwanted heat will have to be found. Unfortunately, we, as operators, are not equipped to adequately study that problem, but we hope someone in this room, where all the capabilities lie, will soon show us the answer.

The second problem about which we are concerned has to do with sputtering on glass. As mentioned before, we have eliminated the use of organic base coats in this process, and it becomes obvious that our next step must be to eliminate any kind of organic top coat. Since our problem is strictly decorative, we are concerned with only two things - the final color and permanence of that color.

The second most used color is silver. Traditionally, this silver color has been achieved by using evaporated aluminum with a clear top coat. We, ourselves, achieve the color by sputtering aluminum, but the oxidation rate is such that a clear top coat is also necessary. By accident we found that a target composed of a much less pure alloy extended the durability of aluminum. Undoubtedly, there are other materials that will not oxidize as rapidly as aluminum which are of the same color. Stainless steel has something of the look, but it is not really bright enough for most designs. Nickel and chromium are also in this category. It is our opinion that the answers to these problems lie not in sputtering itself but rather in

the field of metallurgy. Most alloys are designed for purposes other than color, and it seems that the amount of work done to achieve a particular color through alloy composition is extremely limited.

There are many other colors which are desirable in our field of endeavor, and, again, the answer probably lies in target formulation. It is almost certain that through mixtures of inorganic salts many colors can be achieved. Again, it will require development on the formulation end.

All in all, it would seem to us that a great deal of work is required for sputtering to take its rightful place in our industry. If this work is properly directed and the present problems overcome, there is a huge market available for sputtering equipment. It would seem to us that 80 percent of our processing could be accomplished by sputtering rather than by conventional methods of deposition. When one considers that our segment of the industry is only a small fraction of the total, it becomes apparent that the size of the waiting market is far more than sufficient to justify the effort.

SPUTTER-COATED PACKAGES

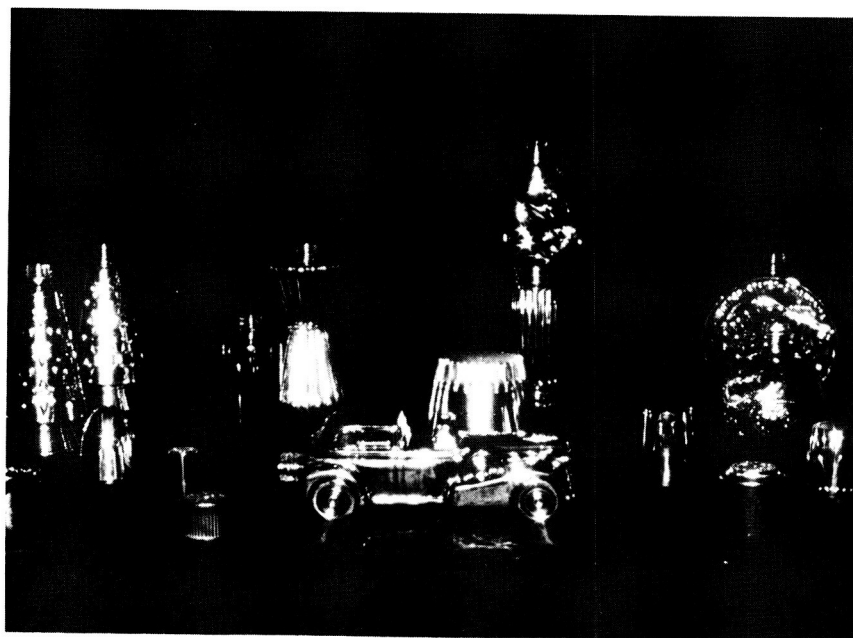


Figure VIII-1

SPUTTERING MACHINE

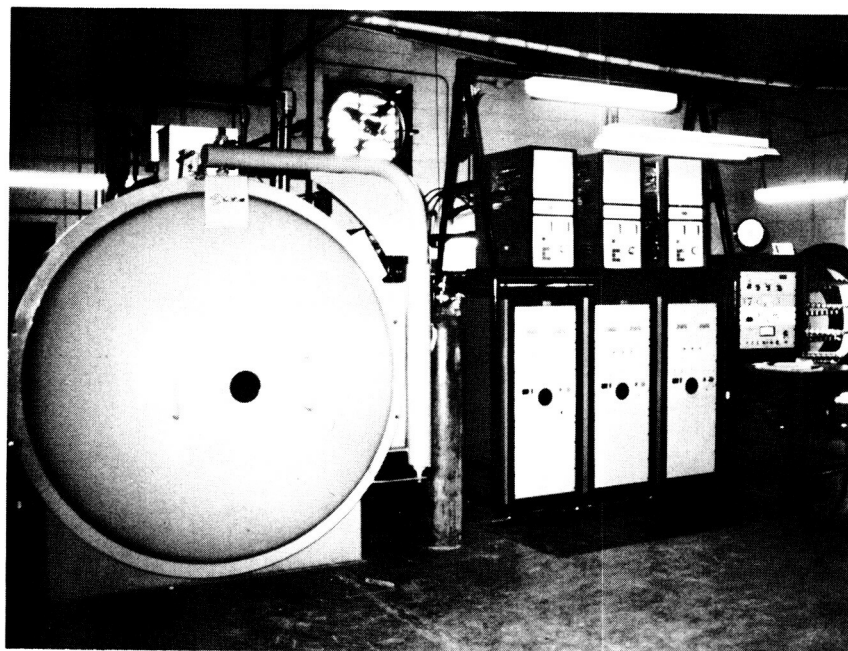


Figure VIII-2

INSIDE VIEW OF CHAMBER

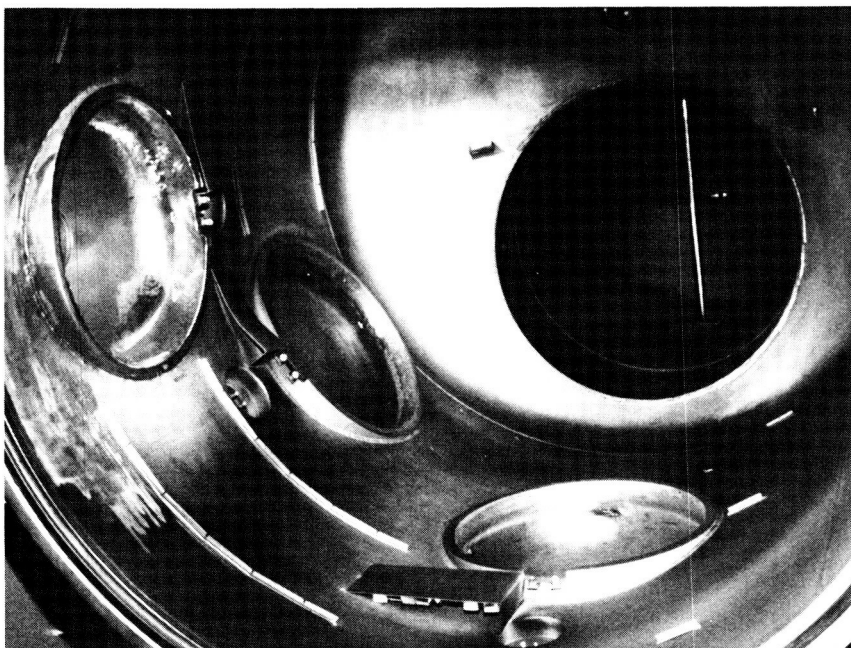


Figure VIII-3

LOAD OF PARTS READY TO ENTER CHAMBER

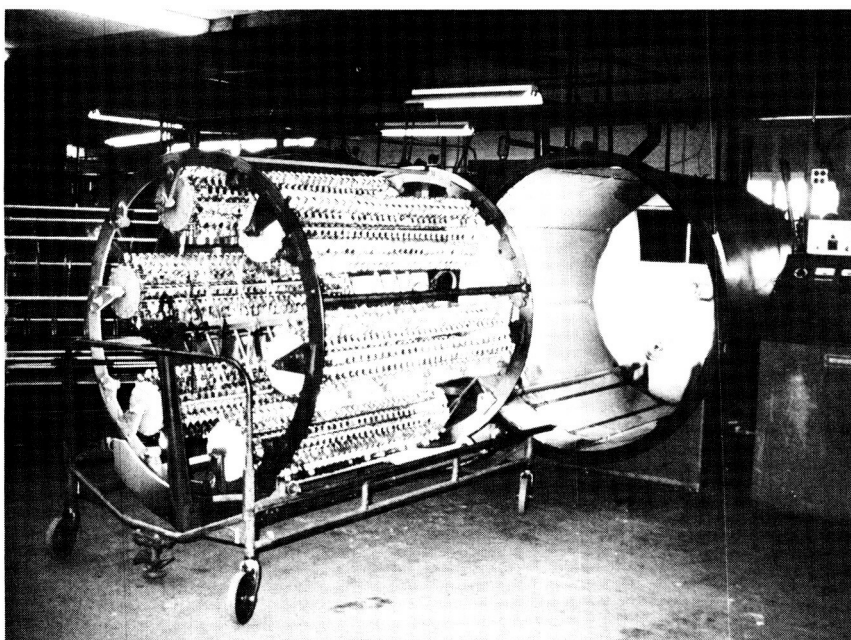


Figure VIII-4

PARTS IN CHAMBER

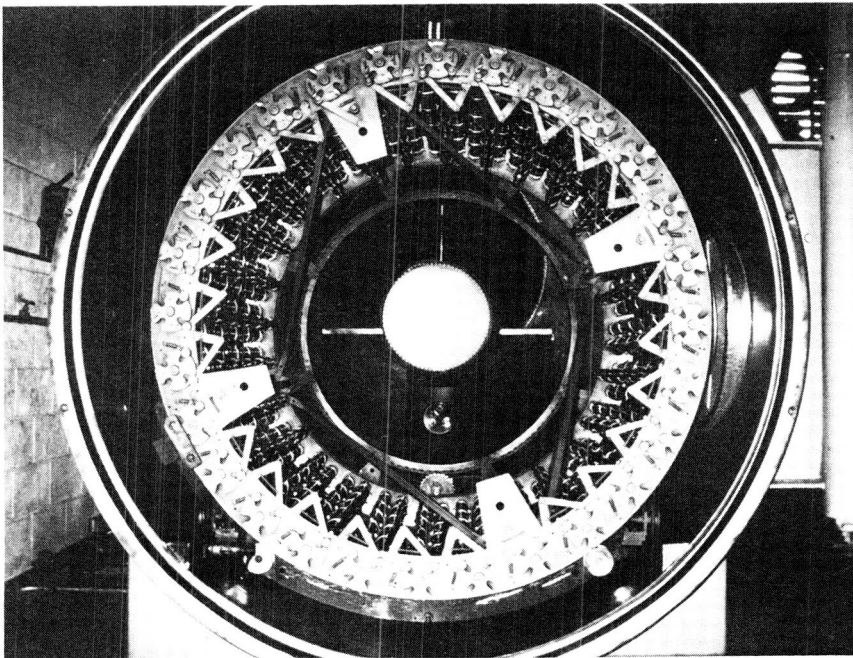


Figure VIII-5

FINISHED PARTS AFTER REMOVAL FROM CHAMBER

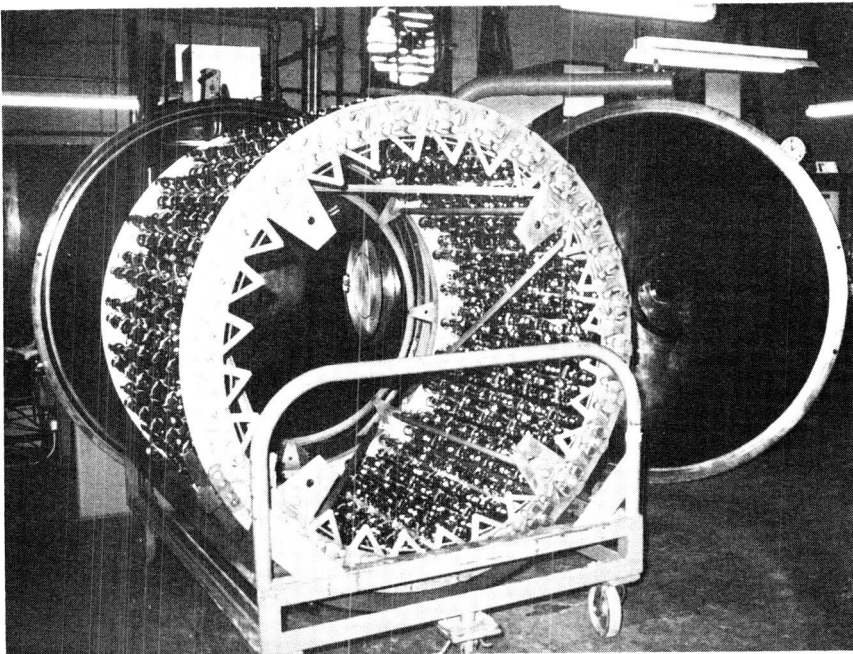


Figure VIII-6

UNLOADING AND RELOADING PARTS

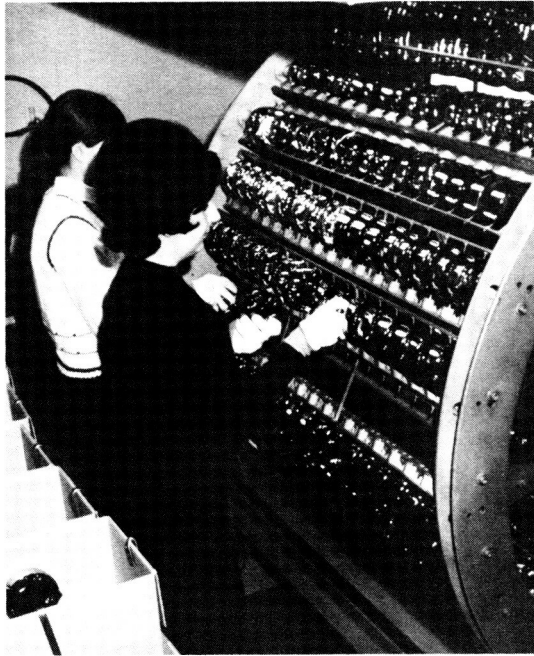


Figure VIII-7

IX. AVAILABILITY OF COMMERCIAL ION PLATING EQUIPMENT

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Manufacturers of thin-film deposition equipment are ready, willing, and able to design and construct commercial ion plating modules and systems. For that matter some ion plating systems have already been produced. Then the question is why is there not "standard equipment"? Why the hesitation on the part of commercial system suppliers to offer general usage ion plating devices? To understand the whys and wherefores, we first must explore ion plating itself.

The mechanism of ion plating has been defined in previous papers at this conference. Equipment configurations have been described as well as a number of applications. Characteristics of electron-beam in comparison with resistance-heated sources have been expressed. What is holding us up?

The status of ion plating today is very similar to that of sputtering 10 years ago. In 1962-63 investigations into the process of sputtering produced impressive data as to what sputtering could do. Imagine, you could now, with sputtering, deposit a thin film of almost any material onto a substrate of almost any other material.

The question then became why should we want to? What could ion plating do for us? "But it's obvious," cried the technologist of the day. At least it seemed so to them. Why then did it take until 1966 for the wheels to start rolling in manufacturers' plants to produce commercial sputtering equipment? (There were homemade modules and systems, as

*Presented by George Unterkofler.

there are ion platers today, but not a significant number.) The answer cannot be stated simply, however. In essence, there was no overwhelming need. Today with the advance of the thin-film integrated circuit technology, beam leads, and even coatings on razor blades, sputtering has defined parameters and defined need. What remains for ion plating is a similar challenge.

Chambers and Carmichael stated, "To achieve a coating (by ion plating) with the desired characteristics, five parameters required control: glow discharge pressure; evaporant flux (electron beam power); substrate voltage and current; source-to-substrate distance and substrate geometry." Certainly these five parameters can be and have, to some extent, been characterized for a large number of materials. Pressure regulators, automatic load control power supplies, E-beam guns, vacuum systems, and similar items are all abundantly available. There is some information yet to be developed regarding the optimum mean-free-path for a given material, substrate, geometry, etc.

We are defining and refining a technology which has great potential but which at this point has too few specifics.

Equipment manufacturers are ready, willing, and able to produce "standard" ion plating equipment. But what form should it take? Should it be E-beam or resistance heated source? Should it be configured for planar substrates or variable geometry (such as solid cylinder or hollow), or both? Are the substrates to be conductive or do we require rf power to bias non-metallic or ceramic substrates? Do we use plasma intensifier field coils? There are many similar questions.

We have stated that the basic components are available; we all know that. Companies are ready to try to supply these components configured into systems and modules as required to develop processes. The challenge is to establish a reasonably fixed set of operational parameters for a given substrate geometry for a specific purpose, such as wear resistant coatings on turbine blades, solid lubricant films on gears and other moving parts, corrosion-resistant protection, and decorative purposes. As in sputtering, all kinds of applications are possible, but it was not until coating razor blades with platinum and chromium became important that Materials Research Corporation (MRC) developed standard radial sputtering systems and modules. It was not until a large electronic producer said we want to process large batches of beam lead devices that MRC produced the largest fully

automatic batch sputtering machine, capable of coating up to 15,000 one-half-inch wafers per batch. It was not until the challenge was met to turn our knowledge into "product" that commercial sputtering equipment became available. MRC manufactured and delivered hundreds of their small, low cost, multitarget rf bias sputtering modules to researchers around the globe once their needs were properly defined.

So it is with ion plating. We are at the threshold of exciting new developments. New and interesting applications will undoubtedly be found as well as solutions to some traditional problems. Equipment manufacturers are eager and willing to work toward the development of ion plating modules and systems. In our own laboratories, we are already doing major investigations into the process. What remains is to first define the limits of the process parameters and then to press through to specific application.

To warrant the engineering required for a commercial system, a definite need and a definite market must be assured. That day is not far off.

DISCUSSION

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I would agree that the field of applications in ion plating has broadened significantly, particularly after the introduction of electron beam evaporative sources in this technique. However, I would like to make the observation that there are commercially available ion plating systems which are specially designed and have been used to plate both metals and dielectrics onto conductive and nonconductive substrates. A specific commercial process does not yet utilize this or any other system but the development of a mature process technology usually takes longer than the 8 months or so since our ion plater was first demonstrated at the A. V. S. show in Boston. This and other similar systems must obviously form the nucleus from which the commercial ion plating process lines must grow.

X. SOME PROPERTIES OF A COAXIAL RF DIODE SPUTTERING SYSTEM

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This paper is concerned with a relatively new form of rf diode sputtering system, namely, the coaxial configuration in which the cathode - the target electrode - is a relatively small diameter cylinder coaxial with a larger anode cylinder. The substrates are afixed upon the interior surface of the anode cylinder and axial magnetic field is provided which may typically be varied from 0 to 100 gauss.

Similar configurations involving magnetron (ref. 1) or inverted magnetron (ref. 2) discharges have been reported in the literature. However, in most cases the electrodes were of such dimensions or arrangement that only a rather small useful substrate area was realized. In 1971 Tischler (ref. 3) described a system with cylindrical geometry for the deposition of decorative and functional coatings on plastics. This system was much like a large normal magnetron but included a transparent cylindrical anode screen of relatively small radius as compared with the radial position of the substrates. Reduced heating of substrates was reported that permitted coating of such heat sensitive materials as ABS plastic, nylon, and polystyrene.

Recent research has demonstrated that, by carefully optimizing the operating parameters of the discharge, one may dispense with the anode screen and mount the substrates directly on a large anode cylinder. This results in substantially higher deposition rates at a given substrate position and reduced contamination in the film. Moreover, the discharge is much more stable at larger electrode spacings. This effectively precludes the

gross instabilities which have been reported in the rf planar diode discharges (ref. 4) and insures good azimuthal uniformity.

GENERAL SYSTEM CONFIGURATION

The coaxial sputtering system (see in fig. X-1) comprises an 18-inch-diameter, 30-inch-high cylindrical stainless-steel work chamber, a sump, which provides the necessary instrumentation and gaging ports, a high-speed rough pumping module, and a turbomolecular high vacuum pump. Electronic instrumentation is housed in a separate cabinet with the exception of the impedance matching network, which is located immediately below the sump through which power is fed to the target electrode.

The target electrode (seen in fig. X-2) is 2 inches in diameter and 30 inches long. Of this, 21.5 inches is actively sputtered. The target is symmetrically ground shielded at both ends by coaxial ground plane cylinders and by annular gridded end planes. This is necessary to obtain the deposition uniformity of which the unit is capable. Even small departures from full cylindrical symmetry may profoundly effect uniformity. High Reynolds number water cooling of the target electrode was provided for maximum reproducibility and to minimize outgassing from any target bonding agent.

The magnetic field is provided by two short solenoids. The field thus produced is uniform within 5 percent over the active discharge volume. For reasons to be discussed shortly, this degree of magnetic field uniformity is necessary to provide good longitudinal uniformity of deposition. Fields up to 100 gauss could be obtained for laboratory studies, but, as will be seen later, commercial systems are usually operated at a field strength of 20 to 30 gauss.

EXPERIMENTAL PROPERTIES OF SYSTEM

A family of experiments were run to determine deposition rates, uniformity, and substrate bombardment as functions of power, pressure, and magnetic field. Both azimuthal and longitudinal uniformity were measured,

and three measurement techniques were employed, namely, interferometry, resistivity, and direct measurement of weight gain. Copper was used as target materials since its films are relatively well behaved. Deposition rate as a function of rf power is shown in figure X-3 with magnetic field as the parameter and in figure X-4 as a function of magnetic field for a fixed power of 1500 watts. In both cases the sputtering pressure was 3×10^{-3} torr, and the substrates were at a radius of 9 inches.

Deposition uniformity performance is given in figure X-5 for variation in the longitudinal direction and in figure X-6 for azimuthal variation in the system midplane. Note that there is a central "belt" over which ± 2 percent uniformity is maintained for variations in longitudinal position. If one rotates the substrates to average out the ± 5 percent variation with azimuthal position, it is readily seen that ± 2 percent uniformity or better can be maintained over a substrate surface area of 450 square inches. Continuing, it is seen that ± 10 percent may be maintained over an area of 940 square inches and ± 18 percent if the entire inner surface of the work chamber, (over 1200 in.²) is used.

Now, let us turn our attention to the matter of substrate bombardment. It has been shown experimentally (ref. 5) that the substrates in rf planar diodes intercept of the order of 10 percent of the power coupled into the discharge and that this power is delivered in the form of energetic electrons produced by ion impact at the target electrode (ref. 6). In the coaxial discharge, however, the cylindrical geometry allows us to easily set up a magnetic field which is orthogonal to the direction of motion. This axial magnetic field causes the electrons to take long spiral paths that eventually intercept the end plates of the anode cylinder. As has been shown before (refs. 5 and 6) the ions in the discharge are relatively unaffected by the rf components of the electric field and their gross motion is determined by the dc components of the electric field. Of course, the magnetic fields used here (up to 100 G) are far too weak to influence the ions. Thus, the substrates are bombarded by low-energy ions, while the electrons go to the end planes to preserve current balance. Retarding potential grid-probe measurements have verified this conclusion and show that the plasma potential, and hence the kinetic energy of the ions bombarding the substrates, is about 30 to 35 electron volts for parameters within the range of interest here. Substrate bombardment power due to these ions as a function of magnetic

field is shown in figure X-7. Bombardment increases with increasing magnetic field because the plasma density increases with increasing magnetic field. Again, current balance considerations determine the observed behavior.

Finally, we may generate a quite important parameter, namely, the deposition rate per unit substrate bombardment. For obvious reasons we want this number to be as large as possible. These data are presented in figure X-8. Note that the function peaks strongly from a magnetic field of 20 gauss. Now, in an rf planar diode this parameter is typically about $1.6 (\text{\AA}/\text{min})/(\text{mW}/\text{cm}^2)$ at best, and one may easily see that there is no advantage to operating at high magnetic fields. Of course, if care is not taken to insure a uniform magnetic field, a larger value will have to be used to insure that the minimum field in the discharge volume is sufficiently large. Evidently, this underlies the necessity for anode screens as in the configuration reported by Tischler (ref. 3).

SUMMARY AND CONCLUSION

The coaxial rf diode sputtering system has been found to be quite useful in depositions that involve large batches of substrates or very heat-sensitive substrates. Such systems are finding increasing applications in the precoating of plastics prior to electroplating, depositions of large batches of substrates through heat-sensitive masks, and even in the coating of knife and razor blades. As the properties of this technique become better understood by production-oriented technical personnel, it seems inevitable that coaxial sputtering will be used in a significant portion of production sputtering applications.

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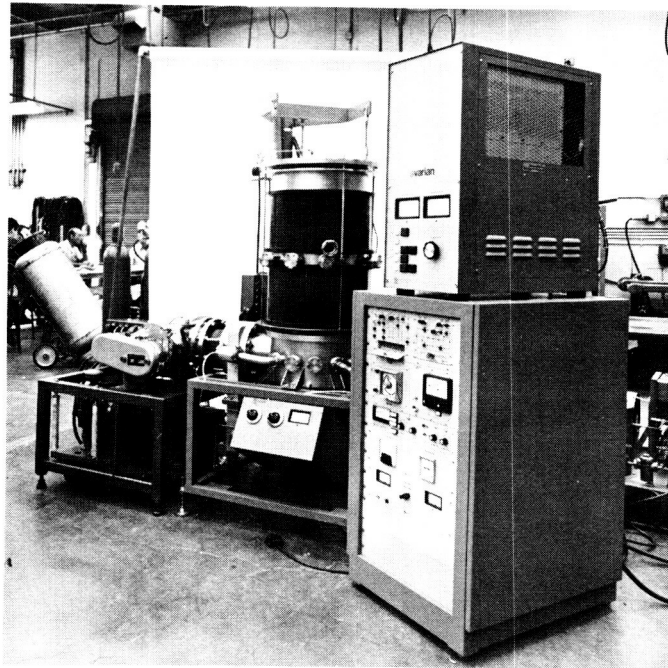


Figure X-1

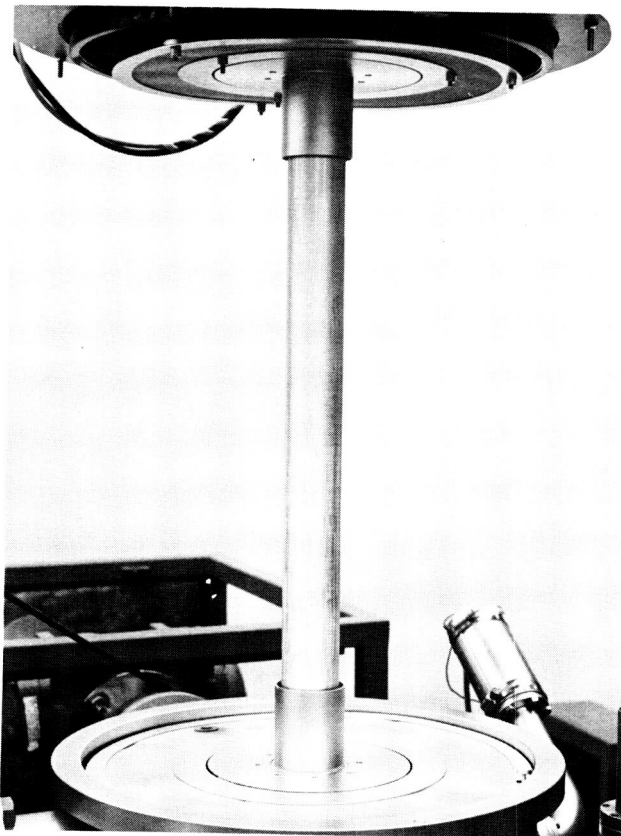


Figure X-2

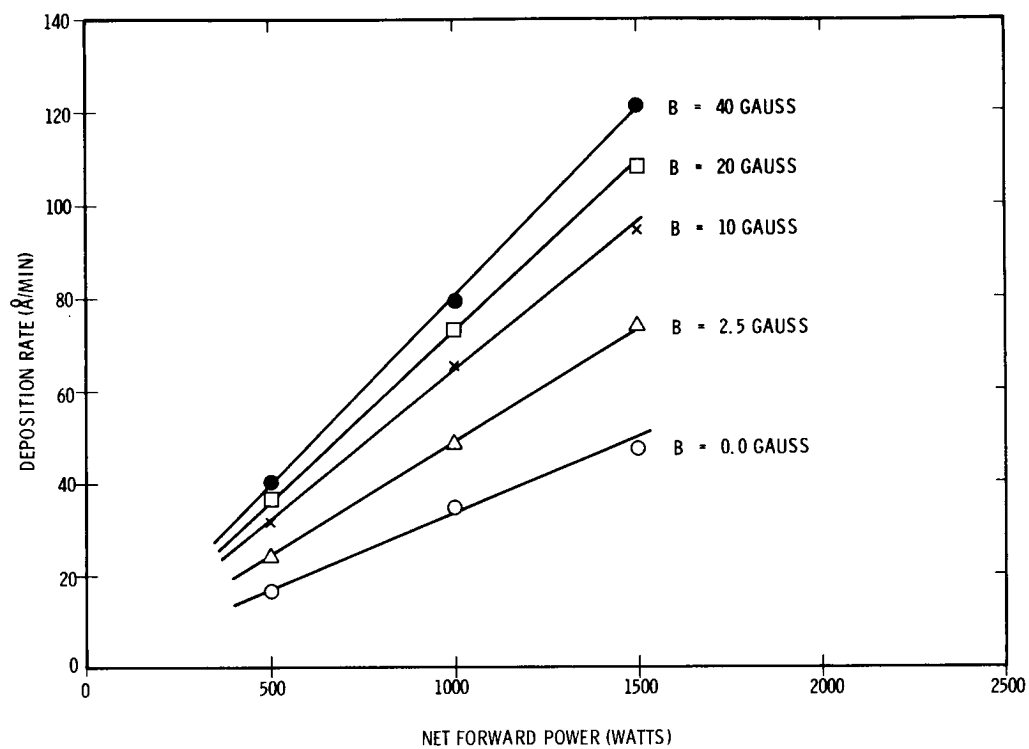


Figure X-3

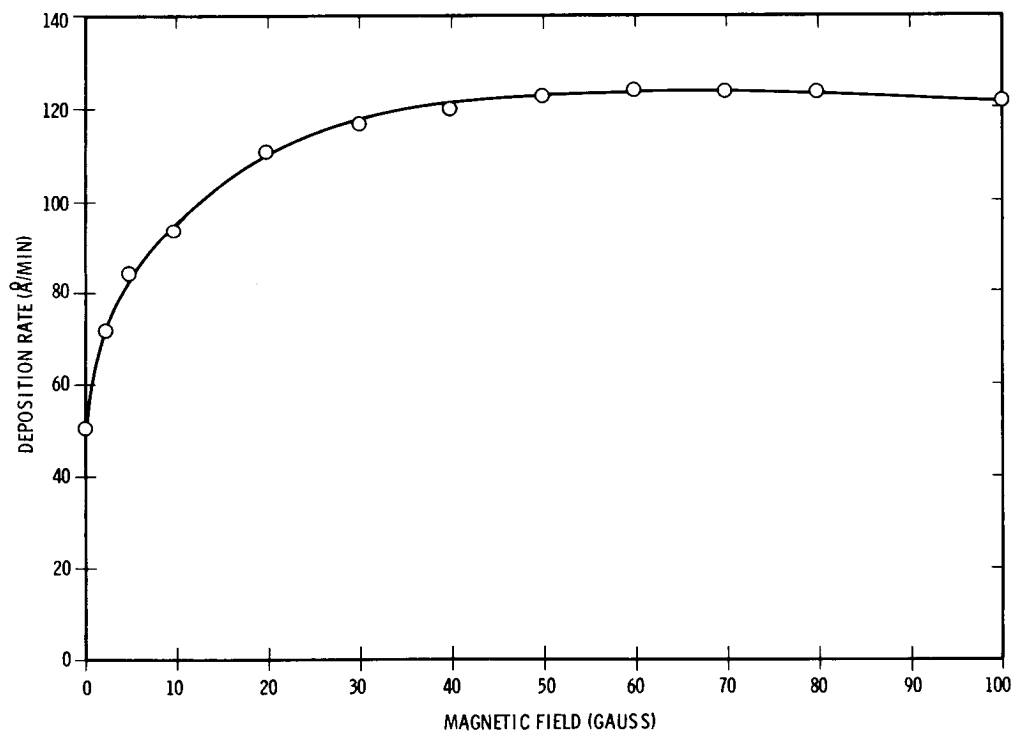


Figure X-4

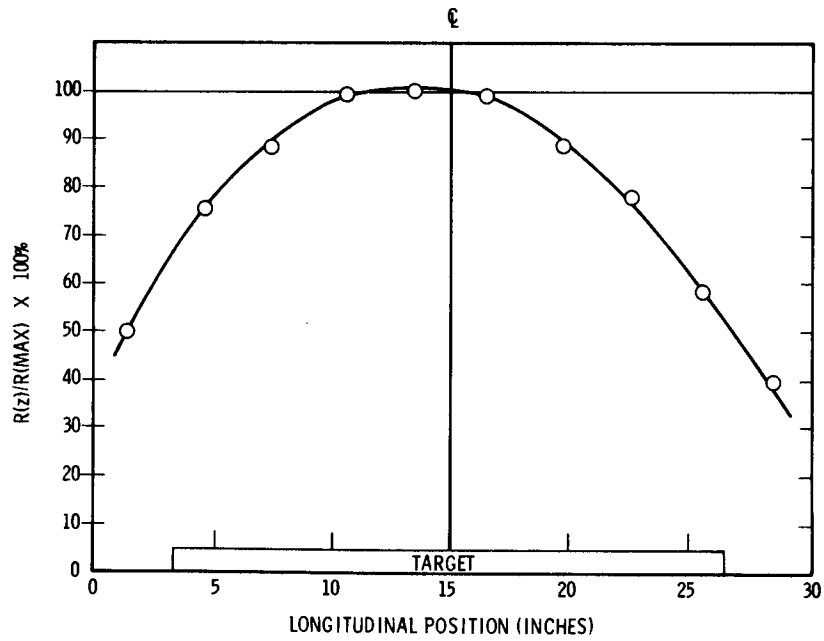


Figure X-5

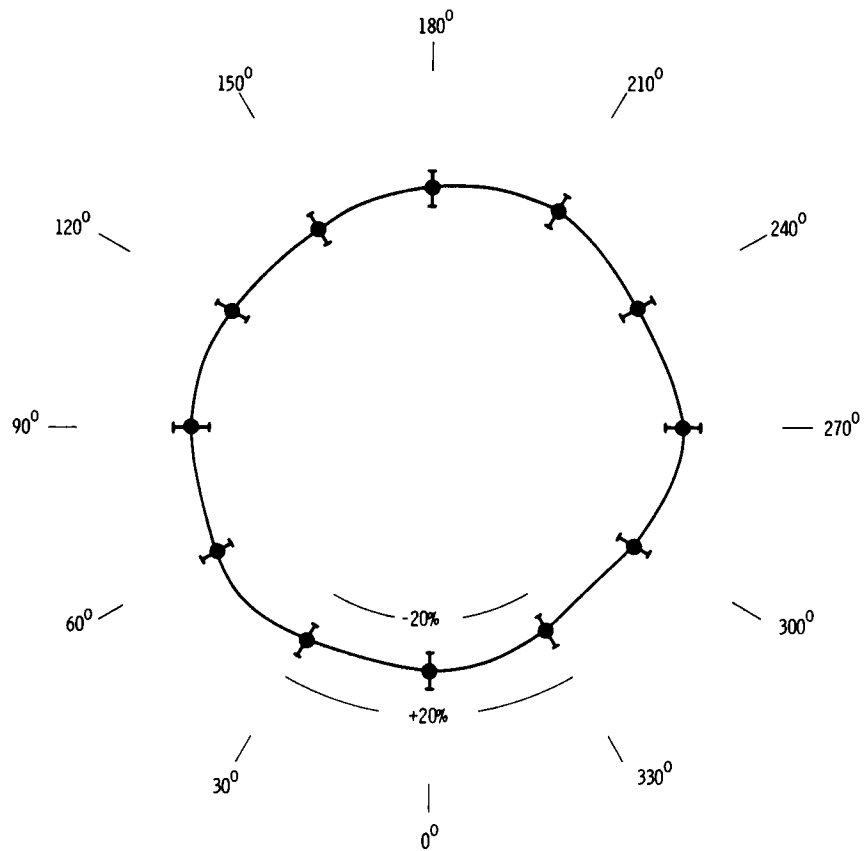


Figure X-6

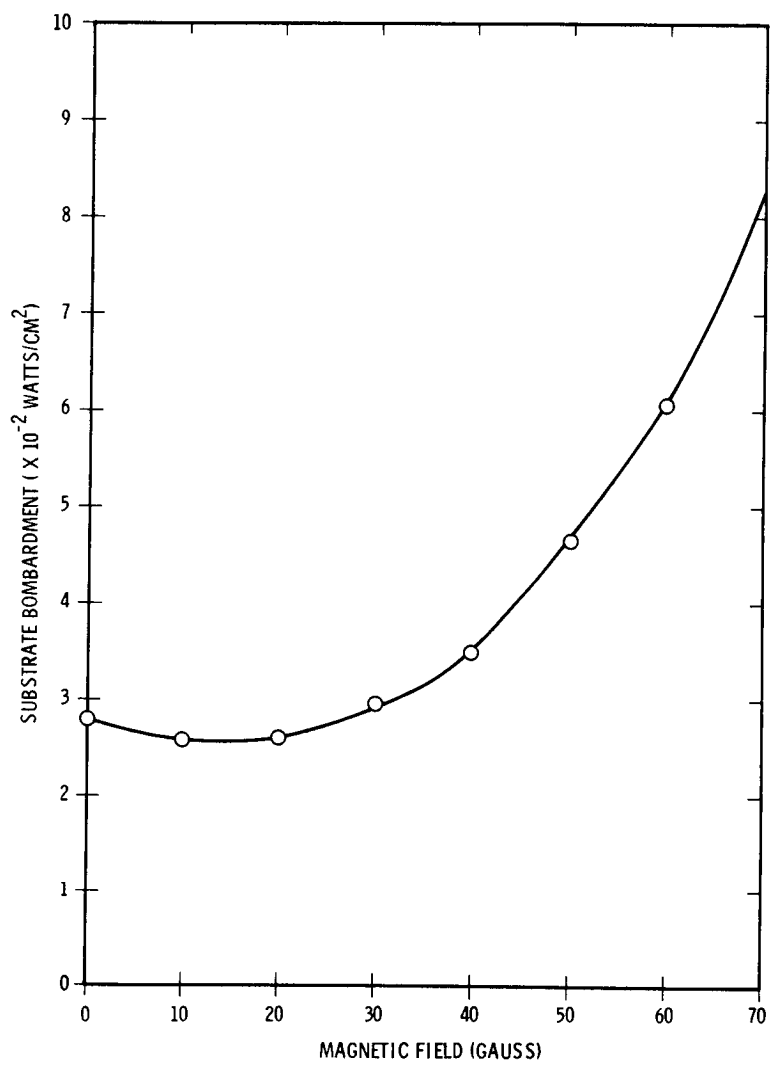


Figure X-7

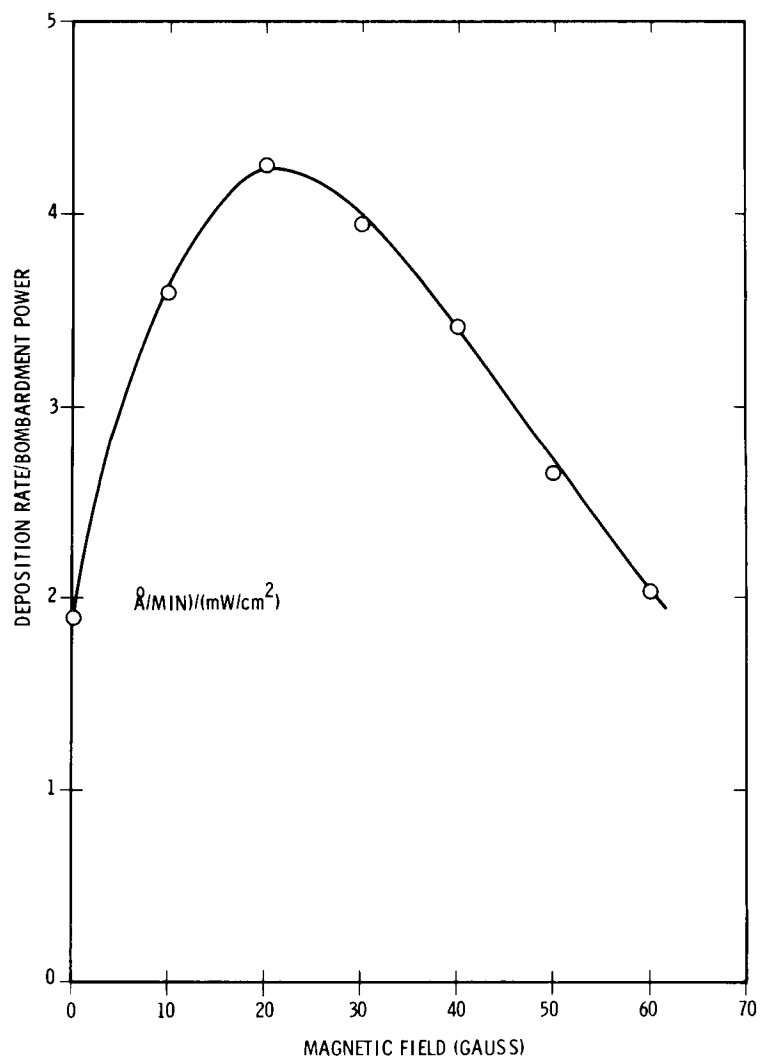


Figure X-8

XI. SUMMARY REMARKS *

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The panel discussion following the formal presentations and the question and answer periods after the individual papers brought out some very interesting points. There were many recurring questions relating to the points listed in the following section. These topics are discussed in the COMMENTS section and reference is made in each topic to the appropriate comment(s) as well as to the contributed discussions by conference attendees, where appropriate. The contributed discussions are given in appendixes A to C.

DISCUSSION TOPICS

1. Comparison of various coating techniques. (See comments 18 and 10 and table XI-1.)
2. Composition of the film with the material we "think" is being applied. (See comments 1, 3, and 4.)
3. The film stoichiometry. (See comments 1 and 3.)
4. Film structure. (See comments 1 and 4.)
5. Contaminants in the film (e.g., other solids, argon, etc.). (See comment 2 and appendix C.)
6. Film thickness and its measurement. (See comments 7, 15, and 19 as well as appendix B.)

*These remarks, unless otherwise identified, are personal opinions of the above three individuals and are not to be construed necessarily as opinions of the rest of the participants.

7. Difference in film thickness on "front" and "back" sides of the specimen. (See comments 8, 9, and 15 as well as appendix C.)
8. Throwing power. (See comments 8 and 15 as well as appendix C.)
9. Lines of force in ion plating and sputtering. (See comments 9 and 15.)
10. Mean free path and elastic collisions of atoms and molecules. (See comment 9 and appendix C.)
11. Epitaxial growth of films. (See comment 4.)
12. Formation of intermetallic compounds during ion plating. (See comment 16.)
13. Limitation on size of objects that can be coated by ion plating or sputtering. (See comment 6.)
14. Economics of ion plating and sputtering versus other modes of film formation. (See comment 5.)
15. Diffusion. (See comments 17 and 11; also comment 2 for diffusion of argon.)
16. Deposition of carbon. (See appendix C.)
17. Interface between film and substrate. (See comments 11 and 14.)
18. Materials which can be deposited as films. (See comment 12 and table XI-1.)
19. Surface temperature during the sputtering process. (See comment 13.)
20. Ionization of plasmas in ion plating. (See comment 20 and appendix C.)
21. Physical processes in ion plating. (See appendix C and comment 20.)
22. Degree of ionization. (See comments 15 and 20 as well as appendix C.)
23. Coating complex parts. (See comments 8, 9, and 15.)
24. Kinetic energy of deposition material. (See comment 13 and appendixes A and C.)
25. Ion implantation versus ion plating. (See comment 14.)

COMMENTS

1. Films of inorganic compounds, such as molybdenum disulfide, deposited by sputtering have been analyzed to determine if, in fact, the film is

the same material as existed in the starting target. A chemical analysis of NASA films has indicated nearly the same composition as in the target (starting) material. The films are dense, pore free, and lack any distinctive substructure. Electron diffraction analysis of the films (deposited under one set of conditions) indicates a film of either extremely small crystallite size or of an amorphous nature. Under other deposition parameters, distinctly crystalline films are identified. Variations in crystallite size with sputtering parameters employed should, therefore, be expected.

2. Argon plasma is used with both sputtering and ion plating. The question frequently arises as to the presence of argon in the film. Generally, the substrate temperature is sufficiently high from the sputtering process that the argon diffuses out of the film and is pumped away. With simple argon sputtering of the substrate at sufficiently high energies, however, argon embedment has been observed with Auger spectroscopy. A mild heating in argon should be sufficient to remove the trapped argon.

3. In the deposition of alloys by ion plating, variations can exist in the composition of the final film particularly with respect to minor elemental constituents. Where the concentration of the minor alloying element is critical, its deficiency in the film can be compensated for by using a starting alloy rich in that constituent.

4. The nature of the film deposited by sputtering can be influenced by the character of the substrate (e. g. , epitaxial growth occurs as deposition starts to take place). This is particularly true with extremely thin films. As the film thickness is increased, the film begins to take on its own characteristic structure and is less influenced by the nature of the substrate.

5. Economically, sputtering can be made competitive with other deposition techniques. This is true once the initial equipment capital investment is made and the comparisons are made on valid grounds (e. g. , multiplicity of pieces to be treated, etc.).

6. The size of objects to be coated with films by ion plating or sputtering is limited primarily by the size of the vacuum system. At NASA Lewis, a vacuum chamber over 120 feet high by 100 feet wide is used in power generation research. This gives some indication of the size of vacuum chambers that can be constructed.

7. Ion plating has been used to deposit films in thicknesses from hundreds

of angstroms to one quarter inch. Free standing parts have been made by ion plating difficult-to-form metals (i. e. , beryllium) onto copper parts and then etching out the copper substrate.

8. The ability of ion plating and sputtering to coat complex geometric surfaces uniformly is influenced by the parameters used in deposition. In general, ion plating will provide better throwing power to coat the back side of surfaces than sputtering. With ion plating, the throwing power will be influenced by the pressure of the gas, evaporation rate of the coating material, and the geometry of the part. With sputtering, the part to be coated must be carefully placed in the plasma so that the plasma sheath envelops the part completely.

9. Frequently, diagrams show the force lines to components to be coated in both ion plating and sputtering as straight lines moving directly from the boat or target to the part receiving the film. It must be remembered that, in the plasma itself, numerous collisions with metallic ions (in ion plating) or the sputtered species (in sputtering). In addition, there are collisions of argon ions with argon and metallic ions or sputtered species with themselves. All of these collisions tend to make the paths to the part to be coated anything but straight lines.

The plasma phase collisions are, however, very desirable. These collisions in part account for the ability of ion plating and sputtering to coat complex geometric surfaces. In vacuum deposition, the mean free path can be made long enough, by keeping the chamber pressure low, to avoid these collisions. It is, however, a direct line of sight deposition process only.

10. In considering deposition by ion plating, it should be remembered that the process is limited to those materials which can be evaporated in a vacuum. If the material dissociates (e. g. , molybdenum disulfide), sputtering must then be used.

11. Ion plating for the deposition of metals and alloys offers the distinct advantage that a diffuse or graded interface can be achieved. Such an interface provides ideal adhesion. This type of interface is generally not obtained with sputtering unless the part is heated during or after deposition to promote surface diffusion.

12. Sputtering with an rf power source offers the capability of depositing a very wide spectrum of materials. These include ceramics, metals, alloys, cermets, semiconductors, and polymers.

13. Some investigators report high temperatures (e.g., 400° C) on the component to be coated by the sputtering process during deposition. Others indicate that surface temperatures never exceed moderate levels (i.e., 90° C). These differences may be related to the mass of the component being coated and the power input levels involved.

Since the ions or species being deposited arrive at the surface to be coated with kinetic energy, this energy is transferred to the surface, resulting in very localized heating. The greater the mass of the coated part and the better its thermal conduction characteristics, the lower will be the resulting surface temperature. Furthermore, the lower the input power, the lower the ion kinetic energy and, thus, the lower will be the quantum energy transferred.

14. Ion plating should be distinguished from ion implantation. The difference between these processes is in the potential employed. In ion plating, the potential is typically from 1 to 5 kilovolts, while in ion implantation, potentials of 100 kilovolts and above may be used to bury ions deeply into a surface.

15. In ion plating, the theoretical lines of force to the various surfaces of the part or component to be coated will not be of uniform intensity. Certainly, these lines will be more concentrated on the side of the part facing the ion source than on the back side or side away from the source. Whether this will make an appreciable or "practical" difference in coating thickness has not as yet been determined.

In addition to differences in the lines of force contributing to differences in coating thickness on complex parts, the degree of ionization of the deposited species will also have an effect. Any evaporant not ionized will deposit in a standard vapor deposition mode. This will result in, or contribute to, variations in coating thickness on complex geometries.

16. With the deposition of metals and alloys onto metal or alloy surfaces, there exists the possibility for intermetallic compound formation. In vapor deposition of gold onto an aluminum surface, gold-aluminum intermetallics were observed to form. With the higher energies associated with such deposition processes as ion plating, such compound formation may be even more likely. Studies are needed to determine the existence of such compounds. As yet, information pertinent to intermetallic formation is scarce.

17. When metallic substrates become heated in the process of sputter deposition, it is possible for the depositing species to diffuse into the surface. The transport process of the incoming species is governed by those considerations involved in normal thermal diffusion. Such characteristics as mutual solubility, etc., will be important.

18. A generalized comparison of various coating techniques is presented in table XI-1. The comparison is made on the basis of a number of characteristics (e.g., materials, nature of the process, film adhesion, uniformity of film, film purity, complexity of surfaces which may be coated, required equipment, etc.). While these comparisons are overgeneralized, they give some idea of the important characteristics of each coating technique.

19. There are various techniques available for measuring the thickness of films deposited by ion plating or sputtering. These include quartz crystal monitors, the optical interference microscope, and holographic interferometry (see appendix B).

20. Some question exists as to the amount of ionization occurring in the plasma of ion plating (see appendix C). Percentages vary from a low of 1 to 5 percent to a high of about 30 percent. The low value is arrived at from theoretical considerations of plasma physics and Langmuir probe measurements of conventional plasma. These low percentages are the result of single component plasma considerations. In ion plating, there are two components, the inert gas (i.e., argon) and the metal, the latter having a lower ionization potential than the former.

Plasma physics research at NASA Lewis with conventional plasma (one component) indicates ionization of from 10 to 20 percent of the neutral atoms. These measurements were made spectroscopically rather than with the Langmuir probe.

Examination of flats coated by ion plating with one of the two faces of the flats facing the evaporant indicates that the back surface of the flat had only 30 percent as much material deposited on it as had the face directly exposed to the source. With standard vapor deposition, only the face directly exposed to the source became coated. It was thus concluded that the material which arrived on the side of the flat not facing the source was in the ionized state.

The diffuse or graded interface achieved in ion plating also argues in favor of percentages greater than 5 percent. It would appear that a care-

fully controlled study of the amount of ionization occurring in the plasma is in order.

21. The generalizations in the summary comment of appendix C are believed to apply primarily to ion beam plating as used at Whittaker Corporation.

TABLE XI-1. - GENERALIZED COMPARISON OF VARIOUS COATING DEPOSITION TECHNIQUES

[Variations in parameters can change some results.]

Characteristic	Coating technique			
	Electroplating	Vapor deposition	Ion plating	Sputtering
Materials capable of deposition	Elemental metals	Elemental metals, some compounds	Metals, alloys, some compounds	Metals, alloys, compounds, cermets, ceramics, polymers
Nature of process	Electrochemical	Vacuum evaporation	Vacuum plasma	Vacuum plasma
Nature of film	May contain pores, can blister	May not be uniform	Dense, pore free, does not blister	Dense, fairly pore free
Adhesion of film to surface	Fair	Poor	Excellent	Good
Type of interface	Sharp between coating and substrate (possible hydrogen embrittled substrate)	Sharp between coating and substrate unless thermally diffused	Diffuse or graded	Relatively sharp
Uniformity of film	Fairly uniform on flats, can have nonuniformity on edges	May vary	Good uniformity	Fairly good uniformity
Film purity	May contain bath salts and gaseous inclusions	Purity of starting material	Purity of starting material	Purity of starting material
Deposition rates	Moderate	Very fast	Very fast	Relatively slow
Film thickness control	Fair	Poor	Excellent	Excellent
Size of object that can be coated	Limited by size of bath and power supply	Limited by size of vacuum chamber	Limited by size of vacuum chamber	Limited by size of vacuum chamber
Complex geometric surfaces	Can be coated but nonuniformly	Only surfaces facing source are coated	Complete coverage of all surfaces	Complete coverage of all surfaces
Equipment required	Chemical baths, controls, and power supply	Vacuum chamber and heat source	Vacuum chamber, heat source, and high voltage supply	Vacuum chamber and dc or rf power supply
Ecology problems	Chemical handling, vapors, and disposal	None	None	None

APPENDIX A

APPLICATIONS OF AN ION BEAM DEPOSITION SYSTEM TO THIN FILM FABRICATION AND MATERIALS COATING

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A technique has been developed and a system constructed which permits deposition of a wide variety of unique thin films on substrates at room temperature. The innovative and fundamental principle behind this system is the fact that the energy for thin film nucleation and growth may be derived from the kinetic energy of an accelerated ion beam of the deposition material rather than by the conventional method of heating the substrate. When ions of the material to be deposited are accelerated in a beam toward the substrate, the kinetic energy of arrival at the substrate is easily controlled, and the thermal energy equivalent can be of the order of $300\,000^{\circ}\text{C}$. Since a high energy of ions at the substrate surface can be so easily achieved and controlled, the growth of well-ordered thin films is more readily accomplished than with the conventional deposition systems.

Contributing to the uniqueness of this system are two predominant factors:

- (1) The energy of the ions in the beam and the average surface atom (ion) energy are high and are readily controlled.
- (2) Deposition under high vacuum reduces energy loss on the surface and minimizes the usual harmful effects of gas surface layers.

Proof of the system's effectiveness was initially demonstrated by depositing (111) single crystal silicon films on (111) silicon substrates. Later

films have included molybdenum on silicon substrates and an insulating diamond-like carbon film, described in detail below, on silicon, glass, and many other substrates. Deposition of other materials, such as titanium carbide is also possible and requires only the selection of the appropriate electrode materials and plasma gas in the deposition system.

The early results obtained by this deposition technique have been described at several meetings (refs. 1 to 3).

There are numerous applications for this novel deposition system and, particularly, for the diamond-like carbon films. For instance, these films should find wide general application as strongly adherent, transparent, wear-resistant coatings. Areas for such applications include wear-resistant coatings for razor blades and other cutting and machining tools; transparent, protective coatings for optical elements and for artificial gems; and coatings to increase the lifetime of electro-mechanical parts such as tape recorder heads.

Materials such as the diamond-like carbon also have application in the semiconductor industry as thin film insulators and semiconductors.

Almost any material can be ionized for deposition by this technique. It is expected that even common materials will have different properties because of the changed crystallography.

ION BEAM SYSTEM

A description of the deposition system follows: A source of positive ions has been developed for the deposition of thin films. This source can produce positive ions of solid material (such as silicon, carbon, and metals) in addition to positive ions of gases. Figure A-1 shows the construction of the ion source. There are two vacuum regions (a higher pressure one and a low pressure one) separated by a plasma constriction opening used for differential pumping. The diameter of the constrictor opening is about 1.5 millimeters. The plasma source chamber is the smaller one where the higher pressure discharge (about 2×10^{-3} to 50×10^{-3} torr) is used to form the positive ions of materials such as carbon. The discharge in the source chamber is used to introduce the carbon atoms

into the plasma where the high energy electrons can ionize them. As is shown in figure A-1, which is an ion source for carbon films, a hollow cavity in a carbon electrode is used as one electrode, and a carbon post in the center is used as the other. Positive ion bombardment is able to sputter carbon from the electrode. When materials other than carbon are to be deposited, the electrode material is changed appropriately.

Here, both electrodes in the deposition source chamber are made of carbon to reduce contamination. The ion source is normally operated in the glow mode at up to several hundred milliamperes, and an axial magnetic field is used to extend the electron orbits so that the discharge can operate at lower pressures.

By means of an auxiliary discharge, the ions are extracted from the source chamber, through a 1.5-millimeter constrictor opening, to a carbon anode located in the deposition chamber. The auxiliary discharge is designed so that use is made of the axial magnetic field to orient the extracted plasma and to reduce the space charge spreading of the beam. By means of the extraction arc, one has a low-pressure discharge (in the deposition chamber) in series with the higher pressure arc in the source chamber. Figure A-2 shows the associated electrical circuit.

The plasma in the deposition chamber can act as a source of carbon (or other) ions as well as a source of electrons. A negative potential applied to the substrate is used to attract the positive carbon ions.

The ion energy incident upon the substrate can be adjusted by control of the substrate potential. Before deposition, the substrate is cleaned by sputtering for several minutes at -400 volts; most of the substrate depositions occur at about -40 volts. The ion current to the substrate is approximately proportional to the extracted arc current. For the deposition of insulating films such as carbon, an rf voltage is applied to the substrate to prevent the substrate from acquiring a net charge. For metal and semiconductor films a dc bias is sufficient. Deposition rates are typically in the range of 20 to 600 angstroms per minute.

Sputtering of the substrate before and during the film deposition is an important feature of this ion beam technique. In fact, by biasing the substrate sufficiently high, this system can be used for general purpose sputter etching.

Brief Summary of Advantages and Uniqueness of System

This ion beam deposition system is a unique system for the deposition of thin films of a quality and nature not duplicable by other techniques. For instance, it is the only known commercially available system that is able to produce thin films of diamond-like carbon. This particular coating will be discussed in some detail later.

As discussed above, there are two main factors that contribute to the effectiveness of this system. First, a carefully designed differential pumping system permits deposition at very low pressures, typically 10^{-6} torr, while most competitive systems operate at pressures as high as 10^{-3} torr. Thus, in the system film purity is maximized, film adhesion is improved, and energy for deposition is not wasted in gas-ion collisions or in collisions with contaminant gas atoms on the surface. Second, the average kinetic energy (controlled by biasing the substrate) of the deposition particles is high, thereby giving rise to stable, highly ordered, pinhole free films; such complete control of kinetic energy is not possible in systems such as evaporation and sputtering systems where deposition is by neutral particles as opposed to ions.

It should also be emphasized that all depositions with this system are done without heating the substrate. Thus temperature sensitive parts can be coated.

Also by controlling substrate potential, sputter cleaning can be done just prior to and even during deposition. Thus surface preparation is minimal.

The system is extremely versatile in that, in addition to ion beam deposition, it is possible to perform sputter etching and ion plating with only slight system modification. Sputter etching is readily done by using a high-voltage supply to bias the substrate. Ion plating can be done by adding a vaporization source and introducing the evaporant into the discharge in the deposition chamber. Major use of the system to date, however, has been confined to ion beam deposition.

FILM PROPERTIES

By selection of the appropriate electrodes or additive gas the system is capable of depositing any material that can be sputtered at an input power of 7.5 kilovolts and 700 milliamperes or less or any material that can be ionized via gas pyrolysis without introducing harmful contaminants. Typical materials include Si, SiO₂, Al, Al₂O₃, Mo, TiC, and diamond-like carbon.

Most exciting among the films produced to date with this system is the last mentioned above, namely, a diamond-like carbon. This material has been deposited in thicknesses ranging from 10 Å to 2 micrometers and has properties that make it potentially valuable in two main areas - semiconductor applications and application as a protective wear resistant coating on various wear surfaces. Some of the properties of this diamond-like coating are listed as follows:

- (1) Highly insulating - resistivity greater than 10^{11} ohm-centimeters (A graphite form of carbon would, of course, be a conductor and not an insulator.)
- (2) Transparent
- (3) High index of refraction - greater than 2.2
- (4) Able to scratch glass
- (5) Resists hydrofluoric acid
- (6) High dielectric constant (close to 14 for best films)
- (7) At least partially crystalline (X-ray diffraction measurements, performed by an independent laboratory, produced a ring pattern. Two of the three measured d-spacings are close to those of diamond. Very thin films, e.g., 500 Å, appear to be amorphous or to have crystallites less than 1000 Å in size.)
- (8) Resistant to sodium ion diffusion - negligible shift in capacitance-voltage characteristics following rinse in NaCl solution and subsequent bias and heat treatment (This implies a film that has a tight lattice and is nonporous.)
- (9) High adhesive force (The adhesion of ion-beam deposited carbon to a number of different materials has been measured and found to be generally very high; in many cases adhesive strength was about

100 times that of No. 810 Scotch tape. A summary of these adhesion measurements is presented in table A-1. The table presents data for the adhesion of the adhesive to the substrate and for the adhesion of the film to the substrate. The fact that this diamond-like carbon film adheres very well to such materials as silicon, stainless steel, plastics, and diverse other materials as listed indicates that many applications using this insulating carbon can proceed with little concern about adhesion difficulties.)

- (10) Radiation resistant (Detailed tests using a cobalt-60 source have shown the diamond-like carbon film to be radiation resistant. This is of particular importance for semiconductors application. Preliminary work has been done in successfully fabricating field effect transistors using this film as the gate insulator rather than a standard material such as silicon oxide).

APPLICATIONS OF DIAMOND-LIKE CARBON FILM

Semiconductor Application

Properties such as high resistivity, radiation resistance, resistance to ionic contamination, etc., make this material an interesting candidate for general use in the semiconductor industry as a thin insulating film. The possibility of intentionally introducing impurity levels into this material to make it a high-energy gap, high-power semiconductor may also open up other areas of application in the semiconductor field. Results reported in earlier literature (refs. 1 to 3) relate to some of these semiconductor applications.

Protective Coating Applications

The diamond-like nature of this carbon film makes it a very good prospect for use as a hard protective coating on such parts as cutting implements, optical elements, and such electro-mechanical parts as tape

recorder heads. All of these areas are among those presently being explored.

Particularly promising results were obtained when industrial slitting blades were coated with diamond-like carbon. A series of tests was made to determine how coating the edges of industrial cutting blades with diamond-like carbon affects the wear properties of such blades. Both coated and uncoated blades were tested in a paper slitting operation. Results indicated that the coated blades produced a much lower drag force on the paper and took as much as 100 times longer than the uncoated blades to reach the same stage of "dullness."

The instrumentation used for these tests involved the following: the slitting blade under test is mounted at about 45° to the plane of the paper. A motorized drive is used to pull the paper tape at a constant speed (about 77 in./min) past the blade, which slits the paper in half as it passes. For these tests, the paper used was Teletype paper tape manufactured by Eastern Paper Co., and the blades were industrial cutting blades purchased from Amercian Safety Razor Co. (No. 88012).

A strain gage is mounted against the back edge of the blade in order to measure the force experienced on the blade by the paper as it is slit. This drag force is plotted as a function of time on a recorder connected to the strain gage. It should be noted that the force so measured is only a relative number to be used in comparing coating with uncoated blades. An absolute measure of the force of the paper on the blade at the point of contact with the blade edge can be obtained by correcting for the lever arm and angle of the blade, but this is not necessary for the comparative measurements of concern here.

Typical data comparing uncoated with coated blades are shown in figures A-3 and A-4. Two effects are obvious. First, the initial force at time zero on the coated blade is much lower than that for the uncoated blade; the diamond-like carbon film apparently reduces the coefficient of friction. Second, the coated blades do not become dull as quickly as the uncoated blades (see fig. A-4 particularly). The net result is that for a coated blade to reach the same stage of dullness as an uncoated blade (same force of paper against blade) it may take 5 to 10 times longer (as in fig. A-4). The particularly good results in figure A-4 are attributed to the deposition of a more uniform

and slightly thicker film than that represented in figure A-3.

The conclusion, then, is that the lifetime of such slitting blades is improved significantly by coating the edges with ion beam deposited diamond-like carbon. For each application, of course, blade lifetime must be defined. For the above tests a blade was considered no longer useful when the paper being cut began to pull and cut unevenly. The coated blades consistently reached this point at least five times later (usually longer) than the uncoated blades. For this application then, the diamond-like coating looks very promising.

Positive results have also been obtained in tests where plastic eye-glass lenses were coated with diamond-like carbon and tested for increased scratch resistance. These tests consisted of scratching both coated and uncoated lenses with 600-grit silicon carbide particles under controlled conditions. Electro-optical measurements of the resultant haze caused by scratching were then made in accordance with a procedure recommended by the American National Standards Institute. It was found that the coated lenses were at least three times more resistant to scratching than the uncoated lenses.

Other testing of this diamond-like coating is being pursued for such applications as tape recorder heads and various other special purpose devices. The cost for producing such coatings is comparable to that involved in sputtering and ion plating systems.

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1. Aisenberg, S.: The Deposition of Single Crystal Silicon Films on Cold Single Crystal Silicon Substrates. Presented at the 1968 Government Microcircuit Applications Conference (GOMAC) (Gaithersburg, Maryland), Oct. 1968.
2. Aisenberg, S.: The Ion Beam Deposition of Single Crystal Silicon Films on Cold Single Crystal Silicon Substrates. Presented at the 15th National Vacuum Symposium (Pittsburgh, Pennsylvania), Oct. 1968.
3. Aisenberg, Sol; and Chabot, Ronald: Ion-Beam Deposition of Thin Films of Diamondlike Carbon. Journal of Applied Physics, vol. 42, June 1971, p. 2953.

TABLE A-1. - ADHESION OF CARBON FILMS

Substrate	Adhesive	Adhesion of adhesive to substrate		Adhesion of film to substrate		Remarks
		lb./in. ²	kg./cm ²	lb./in. ²	kg./cm ²	
Stainless steel 1	Aron Alpha 202	710	50	710	50	Glue broke
Polished stainless steel 2		2300	162	2200	155	Microscope shows that film lifted from substrate
Strontium titanate 3		1110	78	370	26	Microscope shows that film lifted (preliminary measurement)
[111] silicon		1840 - 3600	130 - 254	925	65	Could not determine with microscope whether film lifted
[111] silicon	Scotch No. 810 tape	-----	-----	1100	77	Could not determine with microscope whether film lifted
[110] silicon		11 - 22	0.75 - 1.5	-----	---	This measurement for reference only
Plastic 4	Aron Alpha 202	95	6.7	100	7.1	Could not determine with microscope whether film lifted
Plastic 5		1600	110	1100	77	Microscope shows that film lifted from substrate
Vitreous carbon 5		1600	110	750	54	
Fused silica 5		1600	110	1290	91	
Pyroceram 5		4100	290	2900	205	
Polished chrome		2600	180	2600	180	
stainless steel		2600	180	1800	125	
		2900	205	2800	198	

COAXIAL CARBON ACR SOURCE FOR PRODUCTION OF CARBON IONS

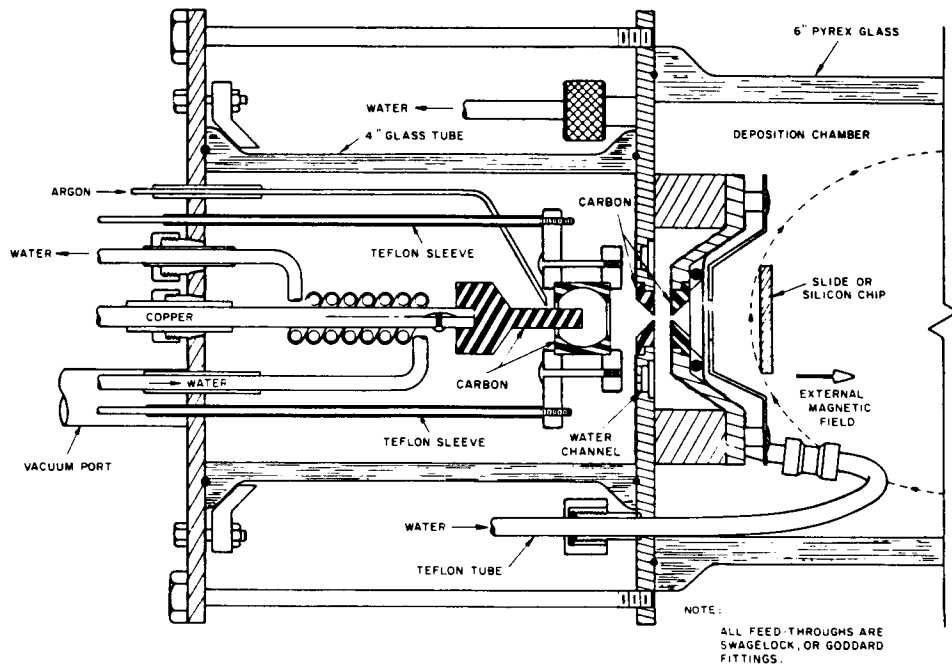


Figure A-1

ELECTRICAL CIRCUIT FOR DC AND RF ION DEPOSITION SOURCE

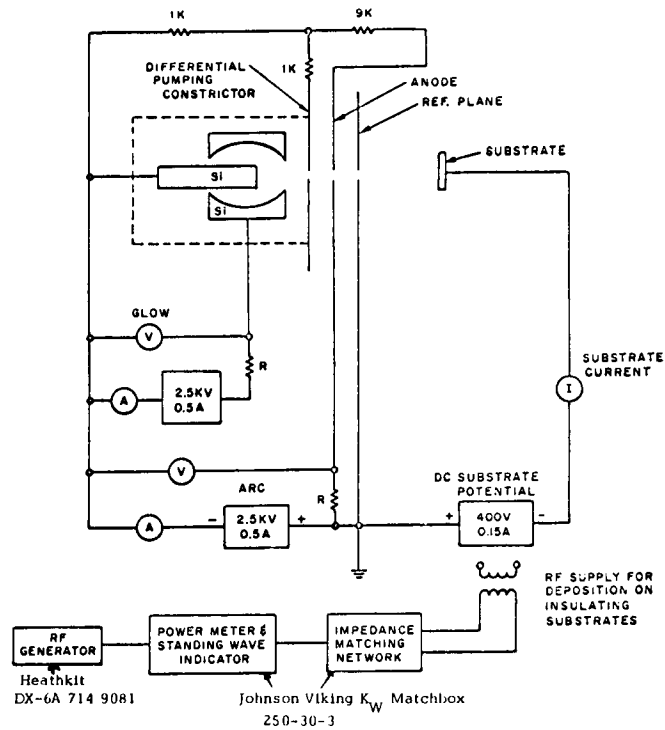


Figure A-2

SLITTING BLADE DRAG FORCE FOR COATED AND UNCOATED BLADE

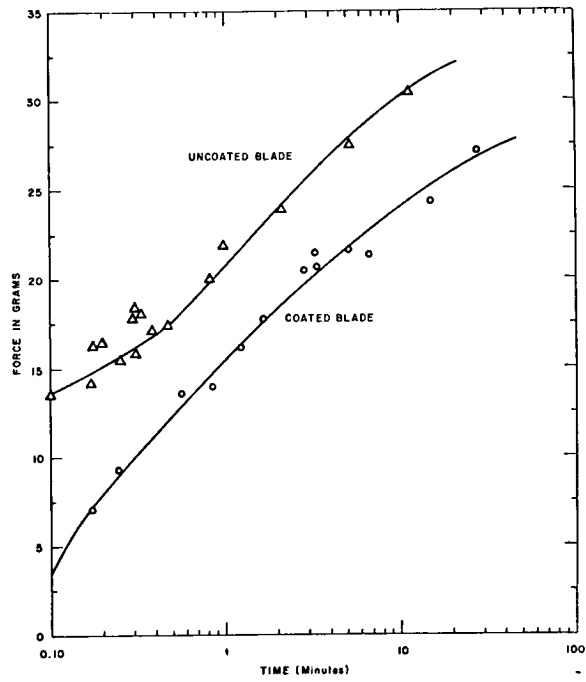


Figure A-3

SLITTING BLADE DRAG FORCE FOR COATED AND UNCOATED BLADE

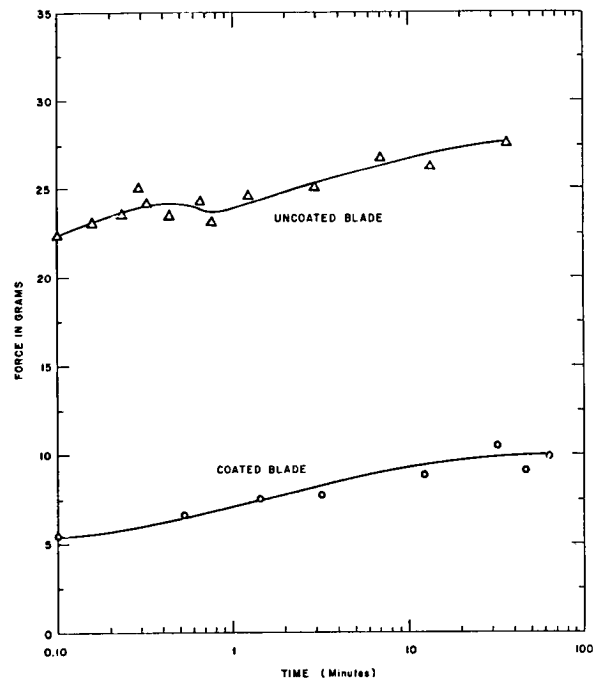


Figure A-4

APPENDIX B

DEPOSITION OF MATERIALS AT HIGH RATES BY ELECTRON-BEAM ION PLATING

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One of the problems mentioned is the lack of a direct film thickness monitor. In principle it has been shown (in ref. 1) that a holographic interferometric technique can be used to monitor the film thickness. Again, in principle, this technique will work well on complex substrate surfaces and can provide dynamic thickness measurements and/or rate of deposition information at several different surface points.

REFERENCE

1. Balasubramanian, N.; Anderson, R. M.; and Stevenson, R. W.: Feasibility of Film Thickness Monitoring by Holographic Interferometry. J. Vac. Tech., May/June 1972.

APPENDIX C

DOMINANT PHYSICAL PROCESSES IN ION PLATING

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A number of processes thought to be important can be shown to be relatively unimportant; while at the same time a number of mechanisms not previously discussed in connection with ion plating will be shown to be of value in obtaining high quality deposits.

Ion plating essentially consists of the following situation: The deposition material is evaporated in a deposition chamber not at a high vacuum but at a pressure in the micron range (around $25 \mu\text{m}$). Along with the evaporation there is a plasma discharge in the deposition chamber and most important, there is a negative potential placed on the substrate to provide for the deposition of a uniquely adherent and non-porous film.

The advantage of ion plating is that one obtains adherent film coverage of the deposition on all sides of the substrate (including coverage into cavities) and also higher deposition rates and thicker films. The uniquely high coverage is very similar to that obtained in electro-plating in electrolytic baths. Normal evaporation in a very high vacuum will only give the usual line-of-sight coverage.

The following are thought to be important processes in ion plating. The evaporated material is ionized in the plasma and because of the electric field lines terminating on all sides of the deposition substrate, the ions of evaporated material follow these field lines and deposit on the front, back, and deep within interior portions of the substrate. The high energy

of the deposition ions also improves the film properties.

There is one important factor, however, that should be recognized in conjunction with the plasmas associated with ion plating. In general, a plasma produced under ion plating conditions and under normal laboratory conditions is not a highly ionized plasma, and the degree of ionization (the ratio of ion density to neutral atom density) is very small. The degree of ionization will usually be less than 1 percent unless the plasma current is very large and there is an intense magnetic field. Thus, we can be relatively sure that the ion density in the ion plating plasma is less than 5 percent of the un-ionized atom density. Since the positive ion density and the average ion temperature will determine the random ion particle current density (and a similar situation is true for the neutral atoms), since the mass of the positive ions is approximately equal to the mass of the neutral atoms, and since the ions and atoms are in approximate energy equilibrium (in the plasma), it can be shown that the random particle current density of the ions to the substrate will be less than 5 percent of the random particle current density of the neutral atoms. Therefore, the large majority of the deposited material is brought to the substrate in the form of un-ionized atoms rather than in the form of ions.

Another way of arriving at the same conclusion is to calculate the substrate ion current and then the mass flow rate associated with this ion current density. It can be seen that, in most cases, the mass rate build up ascribable to positive ion current will not be sufficient to explain the observed deposition rate. Because of the low degree of ionization of the plasma, one can be sure that the build-up of deposition material on the hidden surfaces of the substrate is not due predominantly to the mass transport of positive ions of the deposition material. Also, because of the low degree of ionization of plasmas in general, one can be relatively sure that all of the evaporation material is not ionized but that a good portion of the material reaches ultimate deposition sites without being ionized.

Agglomeration of some of the deposition material into small particles is important in evaporation at poorer vacuums. Normally, when one deposits by vaporization, pressures in the 10^{-4} to 10^{-6} range or better are required in order to get good, bright mirror surfaces. As one increases the pressure in the vaporization chamber, the quality of the

deposited material decreases and the deposition substrate becomes granular. At the same time, because of multiple collisions with the gas, the deposition material reaches the rear and hidden portions of the substrate. This is due to the fact that as the pressure is increased, the deposition atoms do not make collisionless line-of-sight passages to the substrate but experience frequent collisions with the ambient gas. These gas collisions give rise to larger throwing power in terms of coverage, but at the same time, the quality of the deposition film is reduced because of the presence of the background gas.

There are three reasons for the ambient gas hurting the quality of the film. The first is that the collisions of the relatively energetic vaporized atoms with the ambient gas reduces the average energy of the deposited atoms and this will reduce the quality of the film. A second reason is the presence of gas contamination on the substrate which limits the film adhesion and limits the ability of deposited atoms to move around on the surface. The third reason, which is even more serious, is due to collisions between deposition atoms and gas atoms resulting in agglomeration of the deposition material. These deposition atoms, which arrive at the substrate as agglomerates, give rise to a nonadherent granular film, which is generally useless for most purposes.

The introduction of ion plating conditions by means of a discharge, however, has a beneficial aspect in several ways. The deposition material is still vaporized into a high pressure region and a portion of this material forms agglomerates. Because of the presence of the plasma, however, these agglomerates become charged negatively and are unable to deposit on the negatively charged substrate. Also the negatively charged substrate will attract a considerable flow of positive ions which will supply energy to the surface atoms. The transferred energy and momentum will help surface atoms flow and nucleate into superior films. The transfer of momentum to the surface atoms from the plasma ions will take place effectively whether this momentum is brought by ambient gas ions or brought in by deposition material ions.

The reason for the negative charging of agglomeration will be discussed briefly. It is a fundamental theorem of plasma physics that an insulated surface introduced into the plasma will charge negatively. This

is true because the electron and ion density of the plasma are very nearly the same and the electron mass is much smaller than that of the ion mass. As a result, the random electron particle current density is orders of magnitude greater than the random positive ion particle current density so that an insulating surface introduced into a plasma will receive a much larger random current electron density than random ion current density. The insulating surface will, therefore, charge up negatively to a potential where enough of the incident electrons are repelled so that the net ion and electron current is zero.

Thus, in summary it is suggested that the true processes¹ associated with ion plating are

1. Evaporation of the deposition material into moderate vacuum (in the micron range)
2. Gas collisions of the deposition material to give diffusion, scattering, and covering of hidden surfaces
3. Agglomeration of some of the deposition material into small clumps
4. Negative charging of these small clumps as a result of the plasma present in the deposition chamber
5. Repulsion of these negatively charged clumps from the negative deposition substrate (This removes the tendency to form granular deposits.)
6. Positive ion bombardment of the substrate to increase the average energy of surface atoms to make them mobile enough to move into better crystallographic sites and to give nonporous films and better adhesion.

¹See Comment 20.



EXHIBITS OF COMMERCIAL ION PLATING AND R. F. SPUTTERING EQUIPMENT





Opening Session

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